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THE OXFORD UNIVERSITY PRESS

AMEN HOUSE, LONDON, E.C.4

A RELATION BETWEEN PERMEABILITY AND SIZE DISTRIBUTION OF PORES

T. J. MARSHALL

(*Division of Soils, Commonwealth Scientific and Industrial Research Organization, Adelaide, South Australia*)

Summary

An equation has been derived for the relation between permeability and the size distribution of the pores in isotropic material. If the mean radius of the pores in each of n equal fractions of the total pore space is represented in decreasing order of size by $r_1, r_2, \ldots$, and r_n cm. respectively, then permeability is given by

$$K = \epsilon^2 n^{-2}[r_1^2 + 3r_2^2 + 5r_3^2 + \ldots + (2n-1)r_n^2]/8,$$

where ϵ is the porosity in cm.^{3}/cm.^{3} of porous material, and K is in units of cm.^{2}

By this means, permeability can be calculated from the curve relating water content to suction. This has been tested on published data for flow of air through porous stones and flow of water through saturated and unsaturated sands. Calculated values have been found to agree satisfactorily with measured values over a wide range of permeability.

The Kozeny equation is discussed as a particular case of this equation.

Introduction

EQUATIONS relating permeability to other measurable properties of porous materials are used in the various fields concerned with flow of water, oil, and gases through soils, porous rocks, and industrial products. The first equations to be developed dealt with an 'ideal' porous system composed of spherical grains of uniform size. In his analysis of the pore geometry of such a system, Slichter (1899) found that a conducting capillary tube was triangular in section and that along its curved length it passed alternately through maximum and minimum areas of cross-section of pore. If, however, the capillary was assumed to be straight instead of sinuous and to have a circular cross-section of the same area as the minimum triangular section, the errors involved in these substitutions were mutually compensating and an equation could be derived which related permeability to porosity and particle diameter. Green and Ampt (1912) found that, although it was derived for an ideal system, Slichter's equation applied better to beds of sand grains of irregular shape (which it fitted very well) than to beds composed of glass spheres. Subsequently Smith (1932) showed that Slichter's analysis was at fault because the ratio of an average to a minimum section depends on porosity, and, using the mean triangular section as the basis, he then obtained an equation which fitted Green and Ampt's data satisfactorily. However, he found that a better fit for the sand grains of irregular shape was obtained when the minimum rather than the mean triangular section was used.

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The work of Kozeny, Fair and Hatch, and Carman has led to the wide use of an equation, usually referred to as the Kozeny equation, in which an average size of conducting tube is obtained from the hydraulic

radius (as given by porosity, ϵ, in cm.^{3}/cm.^{3} of bed divided by the surface area, S, of the particles in cm.^{2}/cm.^{3} of bed). This equation is fully dealt with by Carman (1937, 1956), Dallavalle (1948), and Childs and Collis-George (1950). It may be written in the form

$$K = \epsilon^3/S^2k, \tag{1}$$

where K is the permeability in cm.^{2} and k is an empirical constant. The constant, k, is usually given a value of 5, but there is evidence of variation especially in consolidated materials of low porosity (Wyllie and Rose, 1950; Wyllie and Spangler, 1952; Carman, 1956). There is serious difficulty in applying the equation to material containing widely different pore sizes especially when numerous small particles which contribute largely to surface area may together act towards fluid flow as a single aggregate of much smaller area.

With the development of suction and associated methods for measuring size distribution of pores (Richards, 1949), there has come the possibility of using pore size instead of particle properties as the basis for a permeability expression. Childs and Collis-George (1950) have developed an equation which takes account of the various sequences of pores of different sizes when pores are randomly arranged as in a porous system. An empirical factor is required in their equation and this has not been widely tested for constancy in different materials.

Derivation of Equation

In the present treatment, the assumption is made that the rate of flow is controlled by the cross-sectional area of the necks connecting the pores. The cross-sectional area of a neck, when the fit of one pore to the next is perfect, is taken to be that of the smaller pore. Since the fit is often imperfect, allowance is made for a reduction in the size of the neck when the two pores, in random alignment, do not fit perfectly on to one another. A mean cross-sectional area of neck is thus obtained and this is taken to represent that of a tube through which flow occurs. The error in neglecting the widening of the path of flow within pores will be in the opposite sense to the errors arising from the assumptions which will also be made that the necks are circular in section, that there is only one neck at the end of the smaller pore of a sequence, and that the path of flow is not lengthened by imperfect alignment of the necks in the apparent direction of flow. It is also assumed that, in isotropic material of porosity ϵ cm.^{3}/cm.^{3}, the fractional pore area in any plane is ϵ cm.^{2}/cm.^{2} This is discussed by Carman (1956, p. 8) as an acceptable assumption when the pore space is randomly distributed.

According to Poiseuille's equation for stream-line flow, the mean velocity, u' cm./sec., of a fluid in a narrow tube of radius r_t cm. is

$$u' = -(r_t^2\, d\phi/dl)(1/8\eta), \tag{1}$$

in which $d\phi/dl$ is the potential gradient causing flow and η is the viscosity. If the cross-section through a porous material shows a portion, ϵ, to be made up of the cross-sections of tubes of radius r_t, the velocity, u',

in this portion will be equal to u''/ϵ, where u'' is the apparent linear velocity for the porous medium as a whole. Hence

$$u'' = -(\epsilon r_t^2 d\phi/dl)(1/8\eta). \tag{2}$$

In the present solution a value for r_t is found which is appropriate to isotropic porous materials.

If the two surfaces, A and B, exposed by a section through an isotropic porous material are rejoined randomly, the pores on these surfaces will be connected by necks whose area of cross-section can be considered in the following way. Unit area of each of the exposed surfaces can be regarded as being made up of n portions each of the same area, $1/n$, and porosity, ϵ cm.^{2}/cm.^{2}, and each containing pores of one mean radius $r_1, r_2, \ldots$ and r_n cm. respectively, where $r_1 > r_2 > \ldots > r_n$. That portion of surface A which has pores of radius r_1 will in effect contact n portions of surface B each of area $1/n^2$ and each containing pores of one size $r_1, r_2, \ldots$, and r_n respectively. The area of neck resulting from perfect pore-to-pore contacts will be that of the smaller pore. However, the smaller pore can fit against more or less of the solid matrix instead of wholly against a pore on the opposite surface and, on the average, the area of contact will be ϵ times the area of the smaller pore. Hence the mean neck area for each of the n portions of surface B in contact with this first portion of surface A will be $\epsilon\pi r_1^2, \epsilon\pi r_2^2, \ldots$, and $\epsilon\pi r_n^2$ respectively. Similarly that portion of A containing pores of size r_2 will provide neck areas of $\epsilon\pi r_2^2, \epsilon\pi r_2^2, \epsilon\pi r_3^2, \ldots$, and $\epsilon\pi r_n^2$ respectively for another n portions of surface B (each of area $1/n^2$) with which it makes contact. The series is continued in this way until the nth portion of surface A containing pores of radius r_n has been considered. This last portion will provide a neck area of $\epsilon\pi r_n^2$ for each of the n portions of surface B with which it makes contact. The average area of cross-section of neck for all the n^2 portions of surface B is then

$$\epsilon\pi[(r_1^2+r_2^2+\ldots+r_n^2)+(2r_2^2+r_3^2+\ldots+r_n^2)+\ldots+nr_n^2]/n^2$$

or

$$\epsilon\pi n^{-2}[r_1^2+3r_2^2+5r_3^2+\ldots+(2n-1)r_n^2].$$

This area of neck is taken to represent the cross-sectional area of a tube of radius r_t controlling flow through the porous material. Hence

$$r_t^2 = \epsilon n^{-2}[r_1^2+3r_2^2+5r_3^2+\ldots+(2n-1)r_n^2]. \tag{3}$$

On substituting for r_t^2 in equation (2), the linear velocity, u, in a direction normal to any cross-section of the porous material is obtained and is given by

$$u = -\epsilon^2 n^{-2}(d\phi/dl)[r_1^2+3r_2^2+5r_3^2+\ldots+(2n-1)r_n^2]/8\eta. \tag{4}$$

Since linear velocity represents the volume of fluid passing in unit time across unit cross-sectional area of the porous material, this result of the averaging process will be valid only if the averages are in all cases based on equal areas of the porous material. This condition has been met using equal fractions of the pore space as the basis. It is also met in obtaining the average neck area, $\epsilon\pi r^2$, for each of the n^2 portions of the contacting surfaces because each of the uniform smaller pores occupies with its

proportion of solid matrix an equal area of surface and each is assumed to have one neck of radius between 0 and r.

According to Darcy's law for the flow of fluids through porous materials, the linear velocity is given by

$$u = -K\eta^{-1}\, d\phi/dl,$$

where K cm.^{2} is the permeability. Hence, from equation (4),

$$K = \epsilon^2 n^{-2}[r_1^2+3r_2^2+5r_3^2+\ldots+(2n-1)r_n^2]/8. \qquad (5)$$

Equation (5) makes it possible to calculate permeability of porous material from the size distribution of its pores.

One special application is to the flow of liquids through unsaturated material. Here the liquid-filled pores are the conducting pores and those filled with air are excluded from the calculation so that ϵ in equation (5) is replaced by the volume concentration, c (c.c. liquid/c.c. porous material). Unsaturated permeability is difficult to measure and a relation enabling it to be calculated at various concentrations should be of value. Even saturated permeability poses experimental difficulties due to air blockages, leakage between the sample and the container, and the disturbance of the structure in the process of measuring permeability when water is used as the fluid. Pore-size measurements can be made as a routine matter in non-swelling materials by measuring the water withdrawn when the suction on the water is progressively increased. The radius of the largest pores remaining full of water when a suction of h cm. of water is applied is given by

$$r = 2\gamma/\rho g h, \qquad (6)$$

where γ is the surface tension of water, ρ is its density, and g the acceleration due to gravity.

In applying equation (5) it will often be convenient to use the suction in place of the pore radius. From (6), $r^2 = 2{\cdot}25\times 10^{-2}h^{-2}$ at 20° C. Hence substituting in (5),

$$K = 2{\cdot}8\times 10^{-3}\epsilon^2 n^{-2}[h_1^{-2}+3h_2^{-2}+5h_3^{-2}+\ldots+2(n-1)h_n^{-2}], \qquad (7)$$

where h_1, h_2, ..., and h_n represent the suction in the equal classes; h_1, corresponding to r_1, belongs to the class with the largest pores and h_n, corresponding to r_n, belongs to the class with the smallest. In equations (5) and (7) K is given as intrinsic permeability in units of cm^2. K may be obtained for flow of water in the units cm./sec. ('hydraulic conductivity') if the numerical constant is multiplied by g/η. This then becomes $2{\cdot}7\times 10^2$ at 20° C. in equation (7).

Relation of Equation (5) *to the Kozeny Equation*

In the particular case of material of uniform pore radius, r_u, equation (5) reduces to a form similar to the Kozeny equation (1). For pores of uniform size, equation (5) becomes

$$K = \epsilon^2 r_u^2/8,$$

and, if the pores are cylindrical tubes whose surface area per unit volume of porous material is given by $S = 2\epsilon/r_u$, then

$$K = \epsilon^4/2S^2. \tag{8}$$

Equation (8) resembles equation (1), but if they are to be identical the Kozeny–Carman constant, k, in equation (1) must be equal to $2/\epsilon$. If k is given its usual value of 5 for unconsolidated materials (Carman, 1937; 1956), permeability calculated by the two equations (1) and (8) will be the same when $\epsilon = 0{\cdot}4$.

This raises the question of the constancy of k. It is generally accepted that values of k depart seriously from 5 in consolidated materials which therefore cannot be handled by the Kozeny equation unless k is first determined for the material. Even in unconsolidated materials, Wyllie and Gregory (1955) found that k varied inversely with porosity but was about 5 at $\epsilon = 0{\cdot}4$. The present conclusion that $k = 2/\epsilon$ conforms fairly well to their experimental evidence.

Method of Calculation

Values for r^2 or $1/h^2$ for use in equations (5) and (7) can be obtained for each of n classes from the corresponding areas under the cumulative curve for pore space plotted against r^2 or $1/h^2$. However, if n is sufficiently large, r_1, r_2, ..., and r_n or h_1, h_2..., and h_n are given with little error by the radius or suction corresponding to the mean water content of each class (i.e. the median radius or suction in each class).

The method of calculating permeability may be illustrated using the data of Day and Luthin (1956), for Oso Flaco fine sand. The water content, c, at zero suction in their packed sand column was 0·416 c.c./c.c. In order to calculate the permeability at this water content, the median suction, h, corresponding to the middle of each of n equal classes of porosity is read from the suction curve of Fig. 1. In the example given, n is taken as 14, corresponding to a porosity class interval, c/n, which is approximately equal to 0·03. The calculation then proceeds as in Table 1 and the value obtained for the sum of products is used in equation (7) so that

$$K = 2{\cdot}8\times10^{-3}\times(0{\cdot}416)^2\times(14)^{-2}\times102{\cdot}9\times10^{-3}\ \text{cm.}^2$$
$$= 2{\cdot}5\times10^{-7}\ \text{cm.}^2$$

The permeability as measured by Day and Luthin was $1{\cdot}6\times10^{-7}$ cm.^{2}

The larger the value taken for n, the more accurate will be the calculation. However, in the case of the Day and Luthin data, the calculated values of K at $c = 0{\cdot}416$ varied very little when a low value of $n = 8$ and a high value of $n = 40$ were used.

The permeability to water at water contents less than 0·416 (i.e. in the unsaturated material) can be calculated from the data of Table 1. For example if the pores in the first three porosity classes are taken to be air-filled so that the water content, c, is reduced to 0·127 and, if n is taken as 11 instead of 14, the values given for $1/h^2$ in Table 1 can be used directly. The sum of products then becomes

$$(1\times1{\cdot}06+3\times0{\cdot}94+5\times0{\cdot}84+7\times0{\cdot}77+9\times0{\cdot}70+11\times0{\cdot}63+$$
$$+13\times0{\cdot}55+15\times0{\cdot}47+17\times0{\cdot}37)\times10^{-3}\ \text{or}\ 47{\cdot}2\times10^{-3}.$$

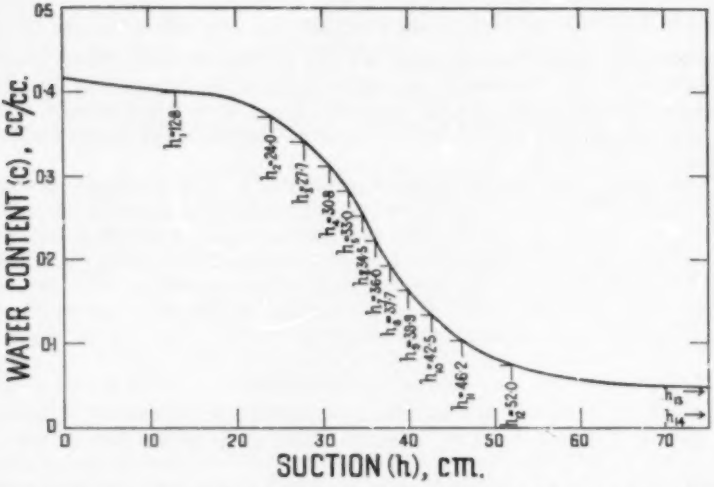

FIG. 1. Water content–suction data for Oso Flaco fine sand. The median suction of each of fourteen equal porosity classes is shown (i.e. n is here taken as 14)

TABLE 1

Calculation of Permeability of a Fine Sand of Porosity 0·416 from the Data of Fig. 1

Porosity class	h	$1/h^2$	*Multiplier*	*Product*
1	12·8	$6{\cdot}11 \times 10^{-3}$	1	$6{\cdot}1 \times 10^{-3}$
2	24·0	1·74 ,,	3	5·2 ,,
3	27·7	1·30 ,,	5	6·5 ,,
4	30·8	1·06 ,,	7	7·4 ,,
5	33·0	0·94 ,,	9	8·5 ,,
6	34·5	0·84 ,,	11	9·2 ,,
7	36·0	0·77 ,,	13	10·0 ,,
8	37·7	0·70 ,,	15	10·5 ,,
9	39·9	0·63 ,,	17	10·7 ,,
10	42·5	0·55 ,,	19	10·4 ,,
11	46·2	0·47 ,,	21	9·9 ,,
12	52·0	0·37 ,,	23	8·5 ,,
13	large	..	25	..
14	large	..	27	..
			Sum of products =	$102{\cdot}9 \times 10^{-3}$

From this, the permeability can be calculated as

$$K = 2{\cdot}8 \times 10^{-3} \times (0{\cdot}327)^2 \times (11)^{-2} \times 47{\cdot}2 \times 10^{-3} = 1{\cdot}15 \times 10^{-7} \text{ cm.}^2$$

At $c = 0{\cdot}327$ the measured value of K from Day and Luthin's permeability data is $1{\cdot}0 \times 10^{-7}$ cm.^{2}

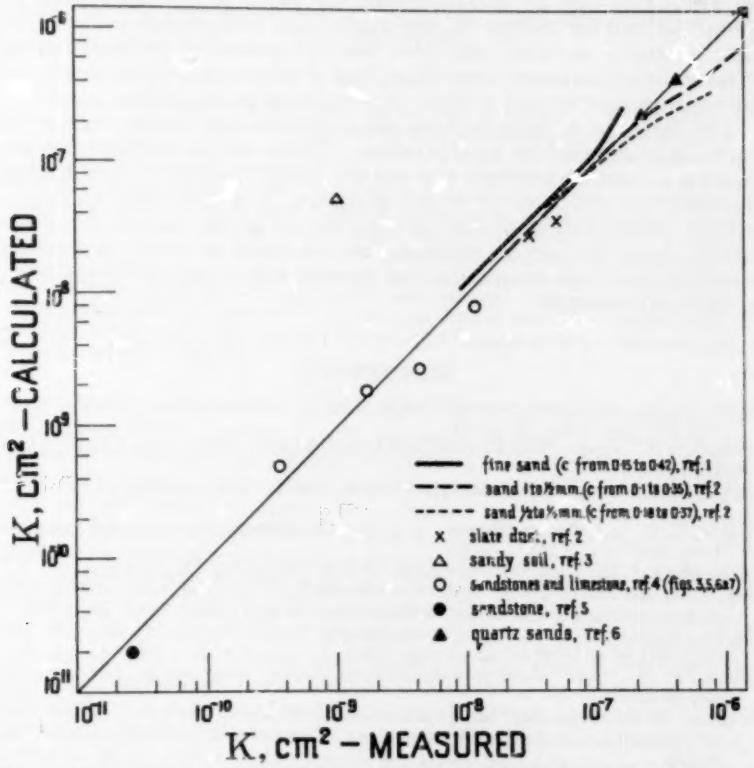

FIG. 2. Comparison of measured permeability with permeability calculated from the size distribution of pores. References: (1) Day and Luthin (1956); (2) Childs and Collis-George (1950); (3) Moore (1939); (4) Purcell (1949); (5) Wyllie and Spangler (1952); (6) Baver (1938), taking 3 in. as the diameter of Baver's permeameter (see Smith, Browning, and Pohlman, 1944, Soil Science, **57**, 197–213)

Comparison of Measured and Calculated Permeability

Permeabilities calculated in this way are compared in Fig. 2 with measured values on sands and porous stones. For this purpose, published data have been used in which permeability and a water content–suction curve of sufficient detail are given for the same material. A large range of measured permeability from $2{\cdot}7 \times 10^{-11}$ to $1{\cdot}3 \times 10^{-6}$ cm.^{2} is represented. Permeability was variously measured using air (refs. 4 and

5 in Fig. 2) or water (refs. 1, 2, 3, and 6) as the fluid and the data from refs. 1 and 2 cover the permeabilities for a given material to water when at various degrees of unsaturation. Agreement between calculated and measured values is satisfactory as is shown by the fit of the data to the straight line representing equality. In any pair of the values obtained by calculation and by measurement, the larger is not more than 2·3 times the smaller except in one case. The exceptional point is for Oakley sand at $c=0{\cdot}23$, and since Moore's measured permeability up to saturation is so much lower than that of other comparable sands, the discrepancy may be due to error in measuring permeability.

The equation appears to have rather general application within the limitations imposed in its derivation. These are principally that the material should be isotropic and should contain no lengthy conducting channels. In order to apply the equation, it is necessary to have a reliable measurement of size distribution of pores and, since this is usually done by suction methods, the accuracy of these in swelling materials may limit the accuracy of the calculation for soils of moderate or high clay content.

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THE CLASSIFICATION OF SOILS

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Summary

There are two possible ways of ordering natural formations: (1) by simplification in order to save time and to make possible an easy grouping by forgoing detailed specification (ordering by one or by a limited number of definite properties); (2) by forgoing simplification and by giving full weight to detailed specification in the establishment of the systematic units, in order to make possible the application of the system in every branch of general and applied science that deals in some way or other with the natural formation to be defined and ordered (ordering by differential diagnosis with no restriction to number or kind of properties).

Both the above systems of ordering are possible with soils. Both are justified, their respective application depending on aims, purposes, and necessities. They could neither fight nor help each other; they are divided from the very beginning by their different principles and goals which lead necessarily to two independent branches of soil systematics.

1. *Introduction.* Under the above title, in a previous number of this Journal, G. W. Leeper (1956) intended to start a discussion on the principles of soil classification. Apparently he expected me to be the first to answer, regarding me as 'the spokesman for the opposition to a matter-of-fact "analytical approach" '. I must say that I never intended to oppose Leeper, and even if he thinks he must fight me because I am applying the principles of a natural system in soil systematics, I do not have the feeling that I must fight him because he does not do so. On the contrary, I am following his attempts with interest, and I can do so, since there is nothing in our respective efforts towards classification which could affect or disturb each other's work. Leeper has given a detailed presentation of the principles of the system he is dealing with, and I might use the questions he has raised to demonstrate the by no means antagonistic differences in principles between his approach and the system which I find indispensable for a rational ordering and placing of the results obtained in my particular fields of study.

I regret there is no other way at the present time than to call Leeper's approach an artificial system and mine the continuation of a natural system already begun by other workers. Leeper strongly disapproves of this terminology, but he did not suggest any new terms himself. The two terms, however, are not invented by me but have been in common use in natural science since 1789, the year L. de Jussieu started the first natural system of plants. They are the only ones in use and indicate the only two principles by which formations in nature can be ordered, leaving perhaps a third possibility of combining or simply mixing the two, which to my belief has little advantage (see section 10).

2. *Definition of an artificial system.* This kind of arrangement is easily defined and explained. It is based on the application of a single

property selected for that purpose or on a small series of definite properties which are settled once for all for the whole system. Artificial systems are simple, easy to handle, and permit a rapid overall view of the formations to be classified, although they are limited by the particular viewpoints given by the properties on which the system is based. The best example is the classification of soils by Albrecht Thaer, based on texture and humus and lime contents.

3. *Definition of a natural system.* Here the classification is not based on a single property or on a series of definite properties, but on all the properties of a formation in nature. By 'all properties' we mean that the soil is not regarded as a complex of a restricted number of properties but as an entity, comprising not only the properties which we know or are able to determine, but also those which will become known at a later stage of soil research. A natural system is therefore never fixed or completed, but is in continuous development; it represents the actual stage of knowledge and reveals the progress of the natural science concerned.

4. *Establishment of systematical concepts.* In the appended diagram I have tried to demonstrate the different methods of establishing classification units by the two different systems of ordering. To demonstrate the principles of an artificial system I have chosen that of Thaer which I have widened by two additional properties. Thaer and his collaborators used in their system a scheme by which they did not limit themselves to the mere statement of 'present' or 'not present' with every property. Without increasing the number of properties they tried to intensify the somewhat limited characterization by giving also the degree of presence of a property on the basis of quantitative analysis. In this sense the pentagon of Fig. 1 represents a unit composed of the following five properties: the texture, the humus content, the depth of the humus horizon, the lime content, and the pH. These properties indicated by black squares are combined by broken lines, meaning that they have been synthesized to a classification complex.

The circles of Figs. 2, 3, and 4 represent soil concepts obtained by the method of a natural system. They are regarded as entities, containing all their properties indicated by small rings entirely filling the circles. All the rings are united by a network of lines in order to express that no one of them is independent, but just a detail of the whole. The circles contain also the properties mentioned in Fig. 1 which are indicated by the same squares, but put into different positions and not arranged in a pentagon. They are present in the same degree, i.e. all four soils have the same texture (silt loam), the same humus content (3·5 per cent.), the same depth of the humus layer (30 cm.), the same lime content (0·5 per cent. $CaCO_3$), and the same pH (7·2). While the Thaer system applies a solid property frame, into which every soil fits, though perhaps in different degree, the natural system tries to pick out those characteristics by which the soils differ most from each other, and which are the most typical and most outstanding in every particular case. These criteria are not of the same kind and they are different in all the three soils of the diagram. By the five-property system of Fig. 1 all soils of the diagram would have to be regarded as the same soil units. According

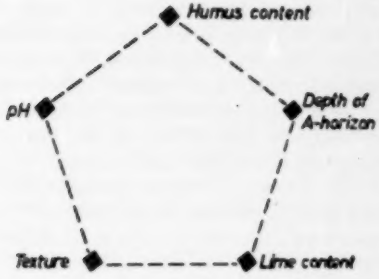

FIG. 1. Artificial classification unit synthesized out of the five properties indicated below. These have been measured and occur in the same quantity in the soils of Figs. 2, 3, and 4, namely:

Texture: silt loam.

Humus content: 3·5 per cent.

Depth of A horizon: 30 cm.

Lime content, surface layer: 0·5 per cent. $CaCO_3$. pH, surface layer: 7·2.

According to a system based upon the above principles (an extended Thaer-system) the soils 1–4 belong to the same classification unit.

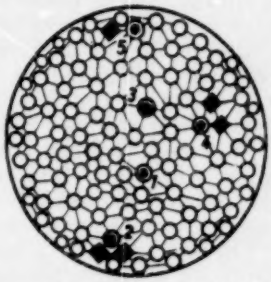

FIG. 2. Solonetz (Hungary). The soil differs from the others most typically by:

1. Specific semi-terrestric soil life and conditions.
2. Soluble salts leached out, but Na-ions adsorbed by the colloid complex.
3. Dense structure with bad aeration and very low permeability.
4. Humus form: anmoor with gyttja-like appearance when covered by water or exceedingly wet.
5. An A/B_h G C profile.

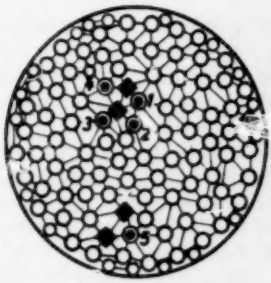

FIG. 3. Chernozem on loess (north-east Austria). The soil differs most typically by:

1. A Ca C profile.
2. Humus form: mull with high activity and excellent humification.
3. Sponge structure with good aeration and good permeability.
4. Original plant cover: grass steppe.
5. Slow weathering, good conservation of the nutrient reserves.

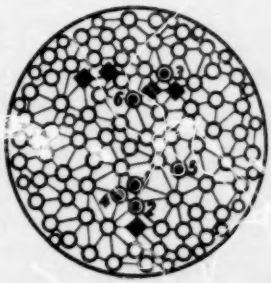

FIG. 4. Tirsified eutrophic rotlehm on diorite (Union of South Africa). The soil differs most typically by:

1. A (B) C profile.
2. Rubefication in the solum.
3. Tirsoid humus form.
4. Low permeability of (B) horizon.
5. Seasonal alternation of extreme wetness and dryness in the solum.
6. High nutrient and iron content brought in by the parent rock.

The systematical concepts 2–4 are formed by free differential diagnosis among all properties of the natural unit without restriction in regard to their kind or number.

to the natural system, however, the soils of the circles 2, 3, and 4 are regarded as three different soil units, corresponding to very different environments, formed under entirely different conditions, representing very different applicabilities, productivities, and values. The soil of circle 2 (solonetz,* Hungary) has almost no productivity and, without appropriate amelioration, cannot support any plant cover, not even weeds; it hardens like rock on drying and is transformed into a structureless mud when wet. The soil of circle 3 (chernozem, north-east Austria) is a very fertile soil, showing high permeability, good aeration, very stable sponge structure, intensive soil life, and excellent mull formation. The soil of circle 4 (tirsified rotlehm* on norite, South Africa) is a fertile soil primarily for sugar-cane crops, but showing dense structure, low permeability, formation of a tirsoid humus with tendency to mull, stagnation of surface water in depressions and on the lower slopes, and developing a grey C_m fragipan below the rubefied (B) horizon.

It is evident that the artificial system, using a property frame into which every soil, whatever it is, can easily fit, gives great advantages where a quick ordering is required. It saves time, simplifies descriptions, is easy to handle for everybody, and does not need any detailed knowledge of soils, except the mere knowledge of the five properties required. There are many usages which also nowadays justify the application of such a system. The times have passed, however, when we *must* use it in all circumstances, i.e. when the knowledge of soils was limited to a few general laboratory properties. The disadvantage of the system of course arises from the fact that the characterization of every soil by only five properties cannot go very far.

Of course the soils of Figs. 2, 3, and 4 can also additionally be characterized by the properties of Fig. 1, or some other properties the analyst finds necessary for his particular purpose, but they are of minor importance for the establishment of the concept of the soil group (global type) or subgroup. I do not by any means underestimate the importance of, for instance, soil texture for classifications for agricultural use, and for this reason I am a supporter of the American principle to form for this purpose a particular category in the system, based entirely on texture (see Kubiëna, 1951, chapter: 'Die landwirtschaftliche Bodenkarte'; Kubiëna, 1953*a*, pp. 543, 547; and Kubiëna, 1953*b*, pp. 8, 9, 21).

5. *Number of properties.* Leeper raises the question: 'How many characteristics must be brought in so as to convert an "artificial" scheme into a "natural" one? Six? Ten? Fifteen?' There is no answer, but the question sounds somewhat as if one would ask, 'How many hairs must be missing before a gentleman has a bald head?'—Is the number important? No, in a natural system there is no prescription, no scheme, either in number or in regard to kind of properties. The essential is that in every individual case the most typical characteristics are actually selected for its definition. In this sense one excellent criterion, i.e. one which typifies it extremely well, is much better than a long description containing twenty poor ones. If one looks only among five routine

* The soil names in this paper correspond to the nomenclature given in *The Soils of Europe*, 1953.

properties for the most typical, possibilities will be very limited. But if one looks for them among all the properties of a given soil without restriction and limitation by a predetermined system one will have the freedom necessary for the establishment of a concept applicable to a natural system. This is the meaning of 'ordering by all characteristics'. Every property, whatever it might be, is free to become one of the leading criteria for the definition of a systematical concept. Finding the typical criteria is usually much facilitated by the fact that these are generally also the most striking, the most outstanding among all characteristics.

It has been a great advantage to me to increase considerably the number of soil characteristics by the application of direct microscopy to the undisturbed soil and by thin-section analysis. Although micromorphological and to a great extent also microbiological criteria are highly characterizing and have always been an indispensable help for diagnosis and for a continuous control of the correctness of my concepts, I have avoided as far as possible using them as leading criteria in my definitions in order to facilitate the diagnosis also by those who are not, or are not yet, in a position to use the microscopic technique for soil diagnosis. This fact makes it difficult to understand how Leeper came to make the statement that my classification is arbitrarily governed by microscopic properties or even by the 'state of the ferric colloids'. In the 167 definitions of different soil formations given in my book *The Soils of Europe*, quoted by Leeper, only five definitions contain microscopic criteria at all and these always in connexion with other non-microscopic properties. In a natural system nobody would be justified in limiting himself to a particular group of properties just because it corresponds to his own particular specialization. Only such an approach and not the number of properties would convert his system into an artificial one.

6. *Natural order in soil formation.* In general, soil scientists believe that soil and humus formation are governed by the conditions of environment which act in particular ways on the inorganic and organic parent materials. We never find chernozems in equatorial Africa, recent rubefied soils in northern Europe, podzols in the semi-desert, or braunerde in the arctic. This principle operates so generally that with particularly suitable parent materials (like loess) even slight variations in the environmental conditions become clearly reflected in profile formation and micromorphology. The discovery of soils as products of the environment due to V. V. Dokuchaev (1879), and of humus and soil formations as typical structural entities, for the first time defined by P. E. Müller (1879), can be considered as the beginning of modern soil research. They laid the foundation of pedology as an independent natural science with its own methods, aims, and contents. But the influence of the habitat is not only shown by the results of regional pedology, but also by the results of the geographically orientated auxiliary sciences like geobotany, plant and animal ecology, climatology, regional geography, regional agriculture, and forestry. It is not just the occurrence and the outer appearance of soils that is ordered according to the nature of the environment; the

ordering goes much further and is recognizable even in the smallest microscopic details. This I have shown in many publications (listed in Kubiëna, 1938, 1948, 1953), and it has also been shown by others. From the micromorphology of recent soils in the most contrasting environments on well-known parent materials it is possible to recognize soils developed under former environmental conditions (relict soils), to study successfully soils which have been destroyed and redeposited on other locations (soil sediments), or soils which have undergone a secondary transformation by the change of the environment. Leeper is against the study of comparative morphology and micromorphology in its dependence on the environment. He writes in his paper: 'All that needs to be done here is to destroy the illusion that there is some "essential order in Nature itself" that we have to discover. If there is, who is to decide which discovery is right?—If four different revelations come, say, to an Austrian, a Russian, an American, and an Australian, are their countries to vote on it? But of course this is all absurd and there is no answer.'

There is an answer, and it is that we have to avoid revelations if we want to get to conformity. What is this so-called 'order' in nature all about? Are theories or revelations necessary to understand its existence? The hatch of a forest bird needs its nest for its development, the nest needs the branch, the branch needs the tree, the tree the forest soil, the forest soil its parent material. One is only possible through the other and we should look in vain for the forest bird in the desert. These interrelations, very common in daily life, continue into the world of the smallest dimensions. As to the natural order found in soil micromorphology, during the last 30 years I have studied it almost daily, in all its available details. In its study I have travelled through nearly seventy states of the Old and the New Worlds. I have been able to establish a great working collection of frame samples of soils and their parent materials, of thin sections, and of coloured microphotographs. The order and its typical dependence shown by Dokuchaev, already visible from profile morphology and from macrochemical and physical characteristics, are even more clearly established by the internal soil life, by the microscopic constituents, their state, their interrelations, and the way they are combined to form a whole.

7. *Checking of systematic concepts.* In a natural system there exists always a 'right' or 'wrong' in regard to the kind of specification and delimitation of a concept. Thus a concept of a soil may or may not fit into the environment of its occurrence, it may or may not correspond to the entity of the environmental factors of a habitat (essentially given by the factors of climate, moisture conditions, topography, parent material, plant cover, animal life, and human influence). Thus one can state that to the subalpine habitats with coniferous forests of the character of a Rhodoreto-Vaccinietum cembretosum occurring on northern slopes of the Central Alps there corresponds the soil concept of an 'iron podzol on gneiss' (or some other acid metamorphic parent rock). If we characterize the soils of these habitats just by the designation of a 'non-calcareous humous sand' we could apply the same concept to a great

number of soils of other habitats showing entirely different environmental conditions. Such a concept lacks sufficient precision, it is too ambiguous, insufficient, and therefore wrong. The existence of a natural order (based on causality) is the objective test of our work in soil systematics that shows whether we have succeeded or failed. Therefore, systematic concepts in a natural system can never be formed in the laboratory only, or by applying arbitrary rules to a few properties from routine research, but by simultaneous and repeated checking of natural habitats.

8. *The question of right or wrong.* The existence of such a question in soil classification is denied by Leeper. According to him the only thing one can do is to try to give satisfaction, and if enough people object one must give in. This is possible in the field of an artificial classification. It is both an advantage and a disadvantage. If, for instance, in the field of artificial classification different revelations—as Leeper calls them—come to a Russian, an American, an Australian, and an Austrian, who is to decide which revelation is right? They are most likely to be different because they are arbitrary. This means that no artificial system can ever become a general soil system forming the necessary combining link between the different branches of research and application of soil science and between the scientists, agriculturists, gardeners, foresters, and soil technologists of the different countries of the world. If we replace the word 'revelation' by a less emotional word, say 'idea', we can state that artificial classifications depend entirely on human ideas. The number of possible human ideas is uncountable, but nature presents to a given fact only one idea, its reality.

9. *The analytical approach.* Leeper thinks artificial systems mean 'matter-of-fact analysis' and regards me as the opponent of the analytical approach. The opposite is true. Every artificial system of grouping is *only* possible by synthesis and by avoiding any kind of analytical approach. The only 'analytical' feature in artificial soil systems is the determination of three or four 'analytical data' (which are obtained by mere determination which, as such, is not yet analysis, i.e. not disjointing an entity by searching for its constructive elements and the way in which they are combined to form the whole). In the natural soil system the application of the method of analysis can and must be extended as much as possible, i.e. it should not be limited only to laboratory properties or even to the soil to be classified as such, but also extended to the interrelations with other soils, to the environment and to other natural formations of a given environment (see section 7).

The better the development of a natural system, the less synthesis is found in it, the more detailed analysis of nature has been done in establishing it. The opposite is true with artificial systems: the more synthesis and necessarily the less consideration of the natural complexity (which is too manifold and too complicated for a rapid grouping), the better the system. The best solution in this respect is given by a system which by application of the most simple means enables the most complete, easy, quickest, and clearest grouping of a great multiplicity of formations to be made.

In former stages of my work I did not fully recognize this important role of analysis (in its wider sense) in soil research and the need to avoid synthesis as much as possible if the aim is the establishment of a natural system of soils and not just a rapid grouping. I must also reverse my former opinion in that I once thought that soil science had fully mastered analysis but had lacked synthesis, because in reality the opposite is true.

10. *Purpose of a natural system.* Of course no system of ordering can be entirely without synthesis. Even the best developed natural system is not nature itself and is not supposed to be, but is just an adequate means for studying nature, for mastering its great variability through the possibility of grouping and determining natural formations in sufficient detail so that it can be used uniformly in every branch of research and application. Its advantage lies in being completely based on objective principles, so that the common subjective influences which, as Leeper has partly pointed out, are so frequent in classification can be avoided—such influences, for instance, as personal ideas, emotions, bias of particular schools or specialization, influence of political or philosophical creeds, of country and district borders, of administrative power, national prestige, &c. No judge or arbiter is admitted other than the proof that the concepts really fit into the reality of nature, together with a few rules for the forming of concepts and for a uniform nomenclature. One of the virtues of a natural system lies, therefore, in the fact that no other system except this can unite the most different branches of research and application, can unite the workers of the most different countries and nations, and can make their results more quickly and easily applicable in all fields of specialization.

As already mentioned in section 3, the completeness of a natural system depends largely on the general progress of research in any branch of natural science. The more we progress in soil science and the more we take advantage of the new results in our system, the less necessity there is to tolerate elements of artificial systems in it. The effect in soil systematics is clearly visible. Year by year we can see that the systems of the different countries become more similar; we develop towards each other and not away from each other. We are even nearer to each other than we realize since, in the main units, we differ mostly in names and not in concepts. Therefore one of the most necessary tasks always remains the continuous effort to complete the international synonymology of systematic concepts.

11. *Is a natural system of soils possible?* It is often said that a natural system might be possible with plants and animals, but not with soils. Soils have no chromosomes, no inheritance of characters. But for a natural system nothing more is required in essence than 'ordering by all properties' instead of ordering by one or by a small number of definite properties. Of course the kind of formations to be ordered must show sufficient differentiation and variation. Industrial products like steel, glass, superphosphate, cement are more or less homogeneous bodies, so that they are fully characterized by a few quantitatively determinable properties. A natural system within each of these bodies would be unnecessary or even impossible. But the organization of soils

is so manifold and the variability of its formations so great that simply to apply the investigation principle used for industrial products must be insufficient for their complete and unequivocal characterization.

Must a natural system from its very beginning and in every part show up details of soil genesis or contain sequences of soil development? Is there something more required than just ordering by all properties? The reason why natural systems in their later stages of development show the mutual relationship or reveal something of the general sequence of the formation, of the general stages of evolution of the members, lies in the fact that through the principle of considering *all* characteristics, gradually those produced by genesis and development are also taken into account and brought to the forefront in the pattern of arrangement. In soils, relationship is not produced by inheritance or descent, but it is seen by the clear graduation of morphology and development. However, up to now the differences between systems which take into account the stages of development and those which do not fully regard them exist more or less in arrangement rather than in the nature of concepts.

12. *Soil systematics and tradition.* I do not imagine that 'the job is already done'. On the contrary: every year brings new soil formations about which we had little knowledge before. An artificial system is so simplified that nobody using it needs to be bothered by new soil formations. But those who follow the principles of a natural system, because a schematization would not help them for the kind of work they are doing, have to be conscious that they can contribute to it, but cannot create the whole system entirely by themselves. It is too big a job to be built up by a single person or even by the scientists of one country. The solution in every case can be decided neither by voting nor by a court of appeal nor by personal influence, but only by the real 'down-to-earth' treatment of the matter: by a prolonged and detailed study of soils in nature. The realm of soil formations is so extended that a general system can only develop gradually. It has a slow growth and must therefore rely on tradition. The search for the typical characteristics in every systematic unit must be started from different directions and undertaken by more than one specialist. Sometimes one will be more successful than another in finding the most characteristic criteria or in establishing adequate concepts or in correcting wrong ones. Nobody who realizes what a natural system means will hold the feeling that he can start anew just by himself. We always have to check and to complete the experiences of our predecessors, but the more we try to continue their work, to preserve the continuity of our working field, the greater is the service we render to our science. Every unnecessary rupture with the past, every arbitrary alteration will delay rather than further collaboration between nations and different branches of soil research, and will destroy the necessary connexion of present and future work with the research of the past.

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13. *Soil systematics and soil genesis.* Genesis is not a property; it gives only the explanation of how a property was formed. But the knowledge of the genesis of a property is very important in systematics since only by this can a property or a unit of properties be fully known and

understood. However, systems must be based on properties and not on explanations of their formation. Therefore we cannot just content ourselves with the mere knowledge of a different genesis of a number of externally similar formations, we must search for new characteristics in every unit which enables us to typify them more clearly, to make them distinguishable. On the contrary, however, we are by no means permitted to regard as equivalent soils which have a similar appearance or which have a few routine properties in common but have quite a different genesis. This may be demonstrated by an example quoted by Leeper that during recent years has received our particular interest—the red-coloured soil formations (see Kubiëna, 1954, 1956). In Leeper's paper (p. 59) there is the following statement: 'One reason for classification is to save time and to simplify our descriptions. If many of the soils that we meet have three or four properties in common (say, a uniform texture down the profile, strongly aggregated clay, and red colour) it is sensible to use one short name for them all.' This simplification is justified for an artificial system, but not for a natural one. Soils of red colour, aggregated clay, and uniform texture may have the following different geneses:

1. Rubefication of braunlehm *in situ* (rotlehm formation).*
2. Laterization of braunlehm.
3. Laterization of rotlehm.
4. Hydrothermal decomposition in volcanic regions (the products of which may be accumulated in extended layers).
5. Insoluble red-coloured constituents of limestones freed by solution weathering and accumulated in depressions, on lower hill slopes or valley bottoms (restitution of fossil rotlehm sediments).
6. Rubefication of non-reddish-coloured insoluble constituents of limestones freed by solution weathering (terra-rossa formation).
7. Soil formations on red-coloured parent rocks.
8. Soil formations developed from soils (or their erosion sediments) formed in earlier geological periods (products which in many cases are readily dated) of the characters indicated in Nos. 1, 2, and 3 (relict or fossil soils showing little secondary transformation).

This looks rather complex. As in other natural sciences there are two ways open to the expert to meet the complexity of nature: to facilitate his work by simplifying it, or to investigate it fully. The decision depends on aims, necessities, methods, and specialization. As far as investigation is concerned the matter today is not so hopeless as it looks. In the majority of cases we are already able to recognize the above variations by their well-developed micromorphological differences and partly also by mineralogical characteristics of the decomposition products.

14. *Must genetical knowledge rely on hypotheses?* To forgo genetical investigation would mean to abandon scientific research itself, because describing things in nature without any efforts to understand them means only a beginning of science, not science itself. Genetical research will always remain the principal task in soil science also. Hypotheses

* As to the nomenclature see the note on p. 12.

mean conclusions which are not, or not sufficiently, based on investigation. They are justified where investigations are impossible or difficult. However, they would not be justified by the failure to take proper advantage of a possible analytical approach. Hypotheses are to a great extent unavoidable in geology and palaeopedology. The recent soil cover, however, is entirely open to research in every part of the Earth. The methods available allow us to investigate it down to the smallest constituents. The different genetical stages are found repeatedly in innumerable examples. Their investigation can be completed by experiments, and some processes can even be studied by direct microscopic observations. Of course there have been and will be errors, as with every human enterprise, but no more than in other fields of investigation.

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THE SOILS OF KERMAN, SOUTH PERSIA

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WITH FOUR PLATES

Summary

No mature soils were observed in the area round Kerman, much of which was occupied by lithosols and regosols. The profiles of immature soils on the fine outwash alluvium occupying some of the broad valleys suggested that the zonal Great Soil Group would be a Reddish Desert Soil. Phosphate and potassium levels of cultivated soils on the fine alluvium are adequate or good; the total nitrogen content is low, though higher on cultivated than on uncultivated soils.

Introductory

OVER much of the central Persian plateau the general relation between relief, soils, water supply, and human settlement is fairly uniform, so that in the almost complete absence of published descriptions of the soils of the area it is probably legitimate to generalize from the Kerman[1] basin, *mutatis mutandis*, to the plateau in general. The full topographic catena of mountains—plain—mountains of the Kerman basin may be observed in most parts of the parallel chains of inland basins running from Ardistan to Kerman, and Isfahan to Sirjan (Saidabad). The half-catena mountains—plain—desert occurs round most of the west, north, and east borders of the plateau, across the boundary between the surrounding mountains and the central desert.

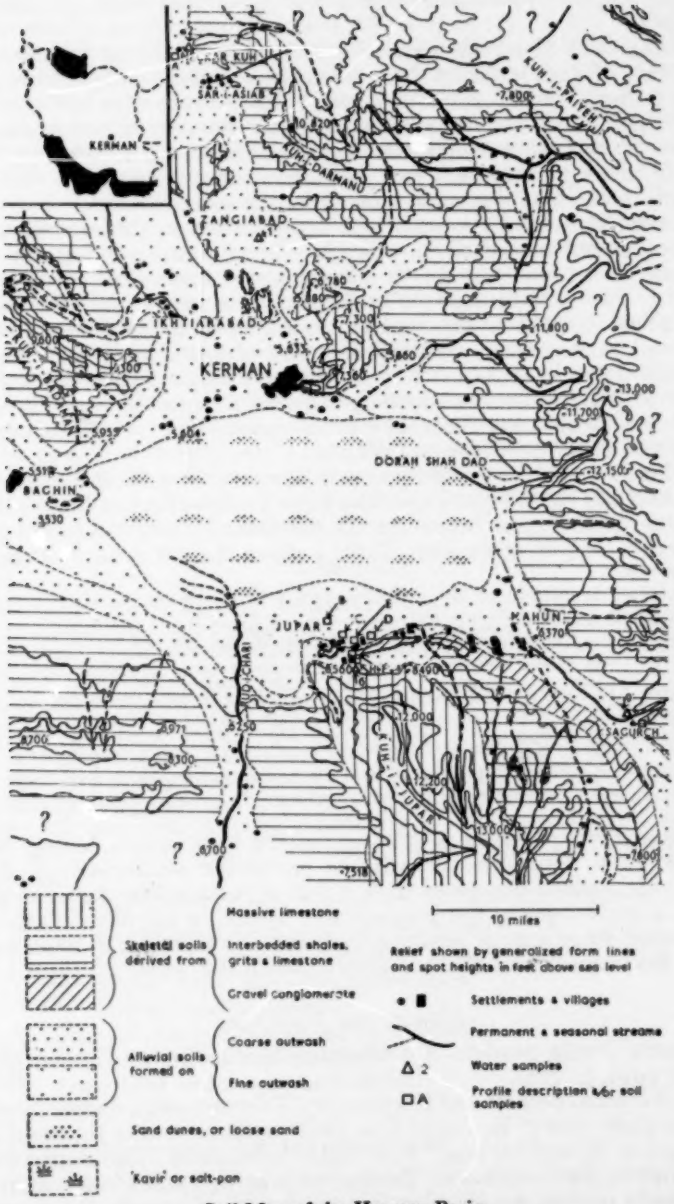
Landscape and Geology

For the purpose of this study the Kerman basin was arbitrarily defined to include parts of two broad valleys, converging on the town and plain of Kerman, and the containing mountains at their junction and highest point (5,000–6,000 ft. above sea level) (see map).

Many of the crests of the surrounding mountains (10,000–13,000 ft.) and the main block of the Kuh-i-Jupar massif are formed of massive red or dark limestones of the middle Cretaceous (Tipper, 1921; Pilgrim, 1924) which rest on interbedded grits and coloured shales, and brown limestone (Upper Lias). The limestones, and the grits or shales when capped by limestone, weather to produce a typical arid landscape in which steep rock slopes rise sharply from stony pediments or outwash fans.

Where not protected by overlying limestones the shales and grits weather to form a broken landscape of low rounded hills, as in the rough foothills of the Kuh-i-Jupar. Further isolated outcrops of Cretaceous limestone form steep hills on the plain, rising 500 to 2,000 ft. above its general level. In the south-east of the basin low rounded ridges of conglomerate and pebbly sandstone form the outer edge of the Kuh-i-

[1] Variously written as Kerman, Kirman, Karman.



Soil Map of the Kerman Basin.

Jupar foothills, and continue as a low ridge from south of Mahun to Jupar.

Conditions of strong physical weathering, combined with frequent showers of high intensity, have filled the mountain valleys with gravel and coarse outwash, and have formed a nearly continuous belt of sloping stone and gravel fans round the foot of the mountains surrounding the plain. Away from the mountains the gravel fans are succeeded by flat or gently sloping sandy, and finally by almost flat fine sandy or silty alluvium, often stretching some miles from the mountains.

Under a cover of vegetation the fine alluvium might have continued to occupy the centre of the plain; at any rate dunes and mobile sand would have occurred only in a limited area downwind of where the Rud-i-Chari stream deposits its load of loose sand. However, almost complete removal of the natural vegetation of the plain for fuel has allowed wind-sorting of alluvial deposits into an irregular sequence of mobile dunes and flat belts of loose coarse sand. Dunes moving in a general easterly and south-easterly direction are now encroaching on the Kerman–Baghin and Kerman–Mahun roads, and on cultivated land near and to the north-west of Mahun.

There are few perennial streams in the area. Nearly all the water for Kerman and the villages is obtained from *qanàt* works (see below) which tap the groundwater below the alluvial fans. Nowhere does the water appear to be critically saline. Table 1 shows the salt content of samples collected:

TABLE 1

Salt Content of Irrigation Water (m.e./l.)

Site	*Source*	Na	K	Mg	Ca	pH
1	Well	15·8	0·39	5·94	7·66	8·42
2	Spring	9·29	0·2	5·57	1·28	8·32
6	*Qanàt*	1·15	0·05	1·24	0·76	8·34
9	Perennial stream	0·75	0·05	0·95	0·55	7·23

Groundwater appears to take up soluble salts and to become more saline, as it percolates through the permeable accumulations of the plain. In general the water from a well is more saline than the water from a *qanàt* tapping the groundwater higher up the alluvial fan, and the water from a deep *qanàt* beneath the fine alluvium is more saline than the water from a shallow *qanàt* beneath the coarse alluvium.

Climate and Vegetation

Central Persia provides a good example of a Plateau Climate (Kendrew, 1949, p. 312).

At Kerman (Beckett and Gordon, 1956) the annual mean temperature on the plain is 62·5° F. (16·5° C.). Daily temperatures in June and July rise to 112° F. and fall to 47° F. at night on the plain. The diurnal range is higher in the mountains. Transpiration is high; calculated values by Penman's method (1948) give an annual total of 30·5 in. from a con-

tinuous crop, and values of 4–5 in. a month during the summer. Winter temperatures are low, with monthly means of 43–45° F. and with daily figures as low as 5° F. Annual precipitation, of which part falls as snow, is 5·8 in. on the plain, and it is very largely confined to the winter and spring. Precipitation in the mountains is almost certainly higher, but no figures are available. Showers are often heavy and occasionally catastrophic.

The natural vegetation of the area shows the expected altitudinal zonation. On the alluvial fans and lower foothills there is a sparse perennial 'camel-thorn' association with *Astragalus*, *Salvia*, *Artemisia* spp., scanty thorn cushions, some succulents, and a few grasses, with a spring flush of annual herbs and bulbous plants. Trees grow only if irrigated or along streams (fig. 3). At about 7,000–9,000 ft. the hill-slopes bear an open scrub of shrubs, thistles, wild rose, and (locally) dwarf tamarisk species. Above 9,000 ft. the scrub is succeeded by a spaced cover of xerophytic mats and dwarf shrubs (fig. 4).

However, in most of the accessible parts the natural vegetation has gone. Heavy grazing by sheep and goats on the alluvial fans and less remote slopes, and ruthless cutting and uprooting for fuel of much of the growth of woody plants accessible to donkey or lorry, have left many parts of the plain without any vegetation and have removed the scrub to leave only the thistles and small herbs in most of the mountain valleys and nearly all the foothills.

The Soils

In regions where physical exceeds biological or chemical weathering, the soils derived from solid parent materials on all but the flattest sites are inevitably skeletal or immature. A soil map therefore becomes an indication more of land form than of soil.

The soils of the Kerman basin are shown on the map (p. 21), prepared from observations made in the summer of 1950. For several parts of the area examination of the soils was perforce cursory and supplemented by recourse to a geological map, but the distribution of the groups of soils mapped indicates general relationships, and the boundaries of group III (the soils of greatest agricultural importance) give a reasonably accurate indication of the areas which could most profitably be irrigated.

The soils are classified into groups on the catenary sequence:

I. *Bare rock and skeletal soils* derived from:
   (*a*) Massive Cretaceous limestone.
   (*b*) Shales, grits, and brown limestone.
   (*c*) Gravel conglomerate.
II. *Soils on coarse alluvium and rock debris.*
III. *Soils on fine outwash alluvium.*
IV. *Loose sand and moving sand-dunes.*
V. *Saline soils.*

I. (*a*), (*b*), (*c*). *Bare rock and skeletal soils*

Outcrops of Cretaceous and Jurassic limestone form steep slopes where they abut on to the plain. The slopes are devoid of soil and

broken only by fissures and dry hollows (figs. 4 and 5). Limestone crests may form a relatively flat cap, or more commonly a saw-edge profile where retreating rock faces have intersected. Apart from small pockets of humose grit beneath the xerophytic mats on the flatter crests and pediments there is no soil formation. Some unvisited areas of brown limestone have been mapped with the associated shales and grits.

Shales and grits weather very much more readily. When capped by limestone they give rise to bare, steep, rubbly slopes, on which scattered small terraces of shaley soil accumulate in the pockets formed by dipping beds of the more resistant strata (fig. 6). In a few areas where the natural vegetation is more or less untouched, thin soils have developed from the shale on quite steep slopes (fig. 4). The slopes are weakly terraced by frequent tracks of the wild goat, but the soil appears to be anchored mainly by scrub, in which wild-rose species are dominant, or by thorn cushions. Salt-bearing beds on the lower slopes of the Kuh-i-Darmanu have led to salt efflorescences on the rocks, and to the notably higher salt concentration of the local groundwater (samples 1 and 2 of Table 1).

When unprotected the shales and grits give rise to broken steeply rounded foothills (fig. 3) dissected by boulder-strewn beds of flood channels and perennial streams, or to the rough uneven landscape of some of the high mountain valleys. The crests of the ridges weather to give shallow, easily erodible, shaley and coarse sandy lithosols, of which the less stony phases are cut by numerous small erosion gullies. Accumulation of alluvium has formed significant areas of stony sandy loam (mapped as coarse alluvium) which are cleared for cultivation in the mountains where there are no other soils which can be more easily cultivated.

On the crests of the gravel conglomerate ridges in the south and south-east of the basin there appears to be some horizon development. In the following profile the persistence of the residues of a thin local gypsum bed, above the horizon of calcium-carbonate accumulation, emphasizes the slight development of leaching processes in the zonal soils.

Site F. On the crest of a conglomerate ridge above Jupar. 40 per cent. cover of stones (1–3 in.).

0–2 in. Very pale brown gravelly calcareous loamy sand; weak clods; no roots.

2–3 in. Light reddish-brown calcareous loamy sand, mixed with nearly continuous crystalline gypsum deposits leached (?) to a vesicular appearance and stained with secondary iron oxides; no roots.

3–14 in. Very gravelly pink loamy sand, larger grains coated with iron oxides; mineral grains and gypsum fragments partially cemented by iron oxides and secondary carbonates.

II. *Soils on coarse alluvium and rock debris*

For the purposes of a reconnaissance survey this group was rather broadly defined to include all alluvial and colluvial soils of which more than half the surface is covered by stones (1 in. or more in diameter). It therefore includes boulder and stone debris (figs. 1, 3, and 6) and soils formed on very stony or gravelly coarse sand on the upper parts of

the outwash fans (fig. 2), and also the soils of areas of moderately stony or stony sandy loam, which are covered by a stony desert pavement.

Two profiles of cultivated soils were recorded:

Site A. Neckar Kuh: terraced fields on steep south-west slope, fallow for 12 months, but irrigated 25 days previously.

0–⅛ in. Surface crust of hard thin plates—the result of recent irrigation, and not typical for local soils.

⅛–8 in. Very pale brown to pink (yellowish red when wet) calcareous fine sandy loam; very weak, soft, medium blocky clods, very friable when wet; numerous fine roots; 'quite dry' 0–2 in., 'moist' 2–8 in.

8–24 in. Very pale brown gravelly calcareous fine sandy loam; hard, coarse blocky clods, pierced by numerous very fine root-holes;[1] small roots to 15 in.; faint white incrustations at 15 in., more marked at 22 in. (also observed on adjacent site not recently irrigated); 'slightly moist' 8–15 in., 'quite dry' 15 in.

24+ in. Gravelly fine sandy loam; a few large roots.

Site G. Sagurch: terraced field on gravelly debris.

0–20 in. Light grey to very pale brown calcareous gravelly to very stony coarse sandy loam; hard, finely porous blocky structure when dry, loose and very friable when wet; roots to 10 in. (gravel 27 per cent. of oven-dry soil).

20+ in. Gravel and stones.

III. *Soils on fine outwash alluvium*

These soils are derived from the loamy sand or coarse sandy loam to sandy clay loam alluvium of the lower part of the outwash fans (figs. 5 and 7). The deposits are variable in texture, and frequently contain gravel horizons below the solum. Sites are normally flat to gently sloping. Rejuvenation of the local drainage pattern leads to marked gully erosion, but normally these soils occur on sites not subject to erosion.

Light-textured soils under cultivation frequently form a weak surface crust. Small parts of the crust (often undercut by wind) may persist for several years after abandonment of a field. Heavier-textured soils form very coarse, hard prisms with slightly rounded tops at the surface during the dry period following the harvest of a winter crop. The thin hard crusts observed at Neckar Kuh (site A) were not usual, and may be the result of the relatively high exchangeable-Na content of the soil. Except on soils annually flooded the crust or prismatic structure is succeeded in due course by a powdery mulch and desert pavement.

Two profiles were described at sites near Jupar:

Site C (i). Jupar: Abandoned fields at northern limit of cultivated soils.

0–2 in. Hard, massive light reddish-brown calcareous sandy loam (dark reddish

[1] The occurrence of numerous very fine pores piercing the clods is very characteristic of soils in this region. Such pores are variously attributed to small insects, bubbles of air expelled on drying, and to fine roots. The discovery of several clods with living roots in the pores suggests that the last and simplest explanation is correct (cf. however, Nikiforoff, 1941).

brown when moist), breaking into medium clods; covered by a thin desert pavement.

2–6 in. Light brown to pink calcareous sandy loam; soft coarse blocky structure when dry; numerous fine pores; no roots.

6–10 in. Light brown to pink calcareous sandy loam; hard coarse blocky structure; some fine pores.

10–12 in. Hard coarse blocky clods, less porous; small carbonate nodules in cracks.

12+ in. Light brown calcareous coarse sandy loam; slightly hard medium subangular structure, weakly cemented by a 'pale red-brown' concretionary material; some carbonate accumulation; dry down to 20 in., very slightly moist below.

Table 2 illustrates the effect of cultivation (irrigation) on the soluble-salt content at adjacent sites on this soil:

TABLE 2

Salt Content of Cultivated Soils (Conductivities of soil: water suspensions (ratio 1:10) measured after 2 minutes shaking. Sites B and C are adjacent)

	Depth (in.):	½	1	2	3	6	7	8	11	12	15	18	20	28
Site	*Condition*	*Conductivity* (mmhos./cm.)												
B	Never cultivated	0·13	..	1·5	..	1·3	..	..	..	..	..	..	..	..
C (i)	Abandoned	..	..	..	0·15	..	0·13	..	..	0·32	..	..	0·44	..
C (ii)	After 2 months fallow	..	0·16	..	..	..	..	0·12	..	0·12	..	0·10	..	..
C (iii)	Irrigated 2–3 days earlier	..	..	0·15	..	..	0·15	..	0·13	..	0·14	..	..	0·15

Dr. M. L. Dewan (private communication) has also made measurements on the soluble-salt content of soils in this area (Mahun) which suggest that moderate salt accumulation below 36 in. in the subsoils of cultivated land is quite common.

Site H. Jupar: abandoned fields immediately south-west of conglomerate ridge, cut by 3–4 ft. erosion gullies heading back from village track.

0–½ in. 50 per cent. surface cover of stones (1–3 in.) over soft medium platey crust.

½–2 in. Very pale brown calcareous loamy sand; soft weak medium subangular structure; no roots.

2–5 in. Calcareous loamy sand; slightly hard moderate fine blocky structure; fine root pores; no roots; slight carbonate deposits.

5–10 in. Very pale brown calcareous loamy sand; hard compact moderate medium blocky clods; numerous root pores; a few large tap roots; increased carbonate deposits.

10–15 in. Hard moderate coarse blocky, breaking into fine blocky clods; numerous fine pores; reduced carbonate deposits.

(Profile dug to 15 in. only.)

Bearing in mind that apparent horizons may be depositional rather than pedogenic in origin, the soils formed on outwash alluvium, though immature, may be taken as the nearest approach to zonal soils in this region. In an area of which the typical mature soil would show carbonate accumulation at relatively shallow depths, it is probably permissible to

describe soils derived from strongly calcareous parent materials as zonal soils. It is possible that even in this area soft limestones and marls might weather to produce profiles more accurately described as rendzinas (cf. Soil Survey of Dimmit County, Texas, pp. 64–65), but no parent materials of such type were observed. Analyses of composite samples are given in Table 3.

TABLE 3

Analyses of Zonal Soils (composite samples)

Site:	*A*	*B*	*C*		*Comments*
Depth of samples (in.):	0–13	0–6	0–8	8–28	Composite samples from several profiles.
Mechanical analysis					
Clay	21·7	15·7	20·5	26·2	Percentages on oven-dry fine earth.
Silt	15·5	5·4	10·0		
Fine Sand	34·7	23·2	32·7	33·4	
Coarse Sand	2·5	39·4	21·7	25·1	
$CaCO_3$	24·6	15·2	14·7	13·9	
Loss on oven-drying	1·5	1·3	2·6	2·2	
Gravel and stones	8·0	8·7	4·3	8·1	"
pH	7·06 (7·1)	7·52 (6·90)	7·45 (6·83)	.. (6·78)	On prolonged shaking. After shaking for 30 min.
Soluble salts					
Na	0·9	1·7	0·2	0·5	m.e./100 g. air-dry fine earth.
K	0·02	0·02	0·01	0·02	
Mg	0·2	0·3	0·02	0·02	
Ca	0·3	1·4	0·2	0·4	
Conductivity	0·41	1·4	0·14	0·20	mmhos./cm.; as for Table 2.
Exchangeable					
Na	0·95	1·23	0·59	0·75	m.e./100 g. air-dry fine earth.
K	0·39	0·48	0·50	0·31	
Cation exchange capacity	6·2	8·8	9·8	10·8	m.e./100 g. air-dry fine earth.
Organic matter	0·9	0·18	0·41	0·17	Percentages of air-dry fine earth.
Total N	0·068	0·024	0·039	0·021	
C/N ratio	7·6	4·4	6·1	4·8	

Mechanical analysis by pipette method; carbonates by Collins's method; pH measured on a 1:10 M/100 $CaCl_2$ suspension; soluble salts dissolved in 80 per cent. alcohol; exchangeable cations replaced by 2N NH_4Cl; cation-exchange capacity by leaching with N K_2SO_4 and estimation of ammonium; organic carbon by Walkley and Black method, assuming a 75 per cent. recovery factor; total nitrogen by Kjeldahl method.

A composite sample of the clay fraction from all profiles gave a cation exchange capacity of 35 m.e./100 g. X-ray examination of the same sample showed the presence of montmorillonite (25%), chlorite (10%), mica (50%), kaolin (15%), and traces of quartz, feldspar, and calcite (?) (percentages very approximate). An electron-micrograph indicated the presence of palygorskite, masked by the mica lines, so that the mica percentage must be an overestimate. Analyses of the solution residues of the corresponding stone fraction did not show the presence of any palygorskite in the soil parent material.

The soils are not mature, and textural differentiation and the development of colour have not proceeded very far.

The horizons of carbonate accumulation are nowhere sufficiently indurated to form the 'crusts' described by Nikiforoff (1937). They occur at varying depths from 4 to 17+ in. Recognizable horizons of 'compaction' (Nikiforoff), apparently due in part to the weathering of minerals to form free oxides of iron, occur above or coincident with the carbonate horizons, but in all cases appear to be permeable and relatively thin. Surface crusts were not observed except for those already described for cultivated soils.

The recognizably reddish coloration, the depth of the horizon of carbonate accumulation, and the hard compact structure of the subsurface horizon, taken with the general appearance of the profiles, suggest that the mature zonal soil would be a member of the world group of Reddish Desert Soils (e.g. Joffe, 1949, p. 239).

The profiles of these soils show many resemblances to the 'Sols Gris-Bruns' described by Lobova (1956), and are indeed classified as such on the Carte des Sols de l'Asie exhibited at the 1956 International Congress. While it is probable that on level areas in the mountains the soil profiles may show rather more pronounced A_1 horizons and greater evidence of leaching, it seems to the author unlikely that there are any significant areas of soils of the Brown or Chestnut groups. Bobek (1951) has stated that under the maple-grove sub-type of this vegetation zone the soils are darker than the prevailing skeletal grey steppe soils, but he has not stated that maple groves occur near Kerman.

The profiles described showed no solonetz character. The high $CaCO_3$ content and moderate clay content of profile A, for example, (Na 15 per cent. of exchangeable bases) are probably sufficient to prevent solonetz development.

The C/N ratios of the soils analysed are surprisingly low, more so than could be accounted for by the arbitrary assumption of a recovery factor for the Walkley and Black determination. There are, however, records of similar low C/N figures of 5–6 for Russian serozems (Bolotina, 1947), and for grey and pink soils of semi-arid regions in India (Satyanarayana, 1946). The low figure, decreasing with depth, may in part be due to ammonium fixation by the micaceous clay (cf. Rodrigues, 1954). The increased total-nitrogen content of cultivated, as compared with uncultivated, arid soils is in accordance with observations on similar soils elsewhere (Smith, 1944), but can possibly be attributed in this case to regular additions of manure, though there is indirect evidence for appreciable non-symbiotic nitrogen fixation on irrigated soils.

IV. *Loose sand and moving sand-dunes*

This group includes the sand-dunes themselves, most of them low and of indeterminate form, moving towards the east and south-east, and the large areas of more or less packed coarse sand remaining behind the dunes. The boundary between sand and fine alluvium was not easily defined upwind of the dunes; downwind the boundary was clearly marked by the limit of the encroaching sand.

V. *Saline soils*

The lowest member of the arid-zone hydrologic sequence was almost completely lacking in this area, lying as it does at the highest point of two valleys. The natural sump for the Kerman basin lies 140 miles to the north-west, in a wide expanse of salt-marsh and salt-pan.

There is a small area of 'Kavir' (salt-pan) by Baghin, with associated solonchak soils. Occasional patches of soils of slightly solonchak character, supporting an obviously halophytic vegetation, occur in small local depressions on the fine alluvium.

Agriculture

The system of agriculture practised in the villages round Kerman is much like that in most arid parts of the Middle East, and is devised so that as few crops as possible are at the stage of maximum water requirement during the period of maximum transpiration in June and July (Beckett, 1957). Cultivation is by nail-plough (cf. Hauser, 1955) or spade to leave a rough cloddy tilth. Fallow fields are not normally cultivated, irrigated, or weeded, but may receive a slight benefit from the manure of sheep and goats grazed on the sparse growth of weeds, in so far as the nitrogen, in particular, and the mineral nutrients are returned in a more readily available form.

The main cereal crops (wheat and barley) and opium poppy are sown in the autumn, irrigated before and after the rains, and harvested in early summer. Millet and barley are sown in late summer and irrigated until shortly before harvest in late autumn. Only fruit trees and vegetable crops such as melon and potato are grown through the hottest part of the summer, to be harvested by early autumn. Yields of cereals appear to be low, averaging a five- to tenfold return on the seed, according to Lambton (1953, p. 365). Irrigation is essential to all crops at some stage of growth.

Water from the few perennial streams and springs in the area is quite insufficient to irrigate all the lands cultivated, and a large part of such water is available in the high valleys or at the head of the outwash fans, where only a limited area is cultivable, as at Dorah Shah Dad and Sar-i-Asiab. On the other hand, the aquifer below the soils most suitable for cultivation is often deep and slow-yielding. So the *qanàt* system (*karèz* in Afghanistan and East Persia; *foggara* in Iraq and Syria (cf. Reifenberg, 1952)) is widely employed, whereby the percolating groundwater is tapped at the head of the outwash fan, where its flow is strongest, and led along a subterranean adit to fields on the finer alluvium.

Briefly, *qanàts* are constructed as follows. After trials a 'mother well' (*madar chah*) is dug to tap the aquifer where groundwater flow is concentrated by a valley, or by buried relief. From the foot of the *madar chah* a long adit (fig. 8), horizontal or gently sloping, is levelled by an ingenious system involving a knotted rope and a bucket of water to strike the land surface at the head of the fields to be irrigated. Frequent vertical shafts (figs. 1 and 7) provide ventilation for the *qanàt*-makers and access for removal of the spoil and regular cleaning.

Qanàts vary greatly in length. Villages such as Jupar, Mahun,

Zangiabad, Ikhtiarabad, and Baghin are watered by *qanàts* 2–5 miles long, from *madar chah* 30–70 ft. deep. Kerman is watered by short *qanàts* from the north and east, and long *qanàts* below the desert, from *madar chah* 300 ft. deep below Jupar and Mahun 14–18 miles away. On the land surface above the *qanàt*, the rings of spoil are quite spectacular. The row of shafts from a long *qanàt* resembles nothing more than the craters from a row of bombs (fig. 5).

Cultivated soils from three villages in the area, and one uncultivated soil, were analysed for common mineral nutrients. The results are given in Table 4.

TABLE 4

Site:	*A*	*B*	*C*	*D*	*E*	*G*	*H*	*Remarks*
Depth of sample (in.):	0–13	0–6	0–8	0–3	3–9	3–5	3–12	
Soluble salts								
Na	0·9	1·7	0·2	0·3	0·1	0·1	0·3	m.e./100 g. air-dry fine earth.
K	0·02	0·02	0·01	0·05	0·01	0·02	0·02	
Mg	0·2	0·3	0·02	0·1	0·04	0·2	0·1	
Ca	0·3	1·4	0·2	0·2	0·3	0·2	0·4	
pH	7·06	7·52	7·45	7·40	7·50	7·40	7·57	..
Total N	0·068	0·024	0·039	0·069	0·067	0·113	0·053	..
Available phosphorus								
(*a*) Bicarbonate soluble	13	..	12·4	19·4	20·6	54·7	17·9	p.p.m. P in air-dry fine earth.
(*b*) Water soluble	0·81	..	0·33	1·32	0·60	7·19	0·79	
Exchangeable								
Na	0·95	1·23	0·59	0·59	0·58	0·48	0·55	m.e./100 g. air-dry fine earth.
K	0·39	0·48	0·50	0·72	0·80	0·70	0·63	
Cation exchange capacity	6·2	8·8	9·8	9·6	10·2	8·5	13·6	..

Analyses as for Table 3; 'bicarbonate-soluble P' measured in 0·5 M $NaHCO_3$ (pH 8·5), soil : water ratio 1 : 20 (Olsen, 1954); 'water-soluble P' measured on 1 : 10 extract (Bingham, 1949). Sites D and E lay on fields under cultivation, north-east of Jupar.

The analyses confirm that, as would be expected, the level of nitrogen is low on all soils. By comparison with the results of experiments on the growth of crop plants on similar soils (Olsen, 1954), available phosphorus (bicarbonate extract) appears to be sufficient; exchangeable potassium is in moderate to good supply (cf. for example *Soils of North Island, New Zealand*, p. 276 (1954)), and there appear to be good reserves of weatherable micaceous minerals in all size fractions. At apparent field capacity the soil at sites C and D has a moisture content of 13–14 per cent. (oven-dry weight), and 10 per cent. at site G.

There are no 'pigeon towers' to collect guano (Dewan, private communication) in the Kerman villages. Dewan reports that round Isfahan, where pigeon towers are common and soils are fairly similar to those of Kerman, yields are said to be increased 50 per cent. by applications of

1·2 metric tons guano (6% N, 2% P_2O_5, 1% K_2O) per hectare. Though lucerne (? species) is grown as an irrigated fodder-crop, local cultivators disagree as to whether lucerne has a beneficial or detrimental effect on a following crop, and, if the former, whether the effect is not due to the manure applied to the lucerne. On the whole the comments by local cultivators on the crop rotations commonly used in the area (Beckett, 1957) suggest that crops grown on local soils would show a response to added nitrogen.

In general the agricultural soils, except where very stony, are not difficult to cultivate. Fields must be irrigated before they can be ploughed. The intractability of stony soils on the higher gravel fans and in the mountains is recognized in the current system of land tenure, which assigns to the crop-sharing cultivators a larger part of the crop from the stony than from the better soils. The soil is readily permeable and, under a growing crop, does not 'cap'. Losses of water by seepage from distribution channels are considerable.

Acknowledgements

Grateful acknowledgement is made to the Persian authorities concerned for the facilities provided for the 1950 Oxford University expedition to Kerman, of whose work this paper describes a part. Acknowledgement and thanks are also due to Dr. A. Muir for his advice both before and after the expedition, and for the clay-mineral analyses; to Mr. Eric Gordon, whose geological map (compiled from all available sources) is the basis of the map to this paper; to Mr. H. H. LeRiche for the analyses of samples of irrigation water quoted in Table 1; to Mr. D. A. Nethsinghe for analysing the phosphate extracts; and to Dr. M. L. Dewan for providing copies of the results of his analyses of soil samples from the agricultural school for the area.

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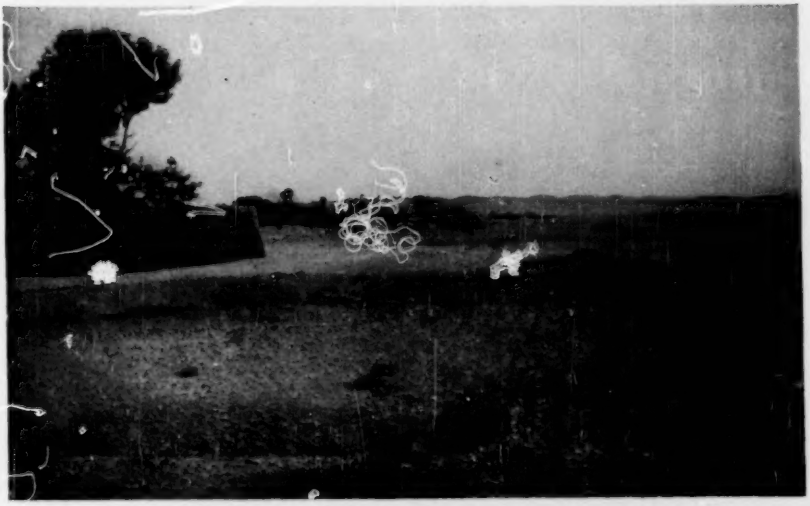
(Received 30 January 1957)

1. Coarse outwash alluvium in the dry valley south of Mahun. Oxford zoologist lowering a plankton net down the shaft of a *qanàt*



2. Stony outwash alluvium by Jupar, cleared for cultivation in centre middle distance. Conglomerate ridge in right background

P. H. T. BECKETT—PLATE I

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P. H. T. BECKETT—PLATE 1

3. Thin stony soils of the foothills north-east of the Kuh-i-Jupar (7,500 ft.) and stony alluvium in the flood valley. Trees are growing only round the reservoir or along the water-channel

4. Thin shaly soils on shales and grits (left and foreground), and bare limestone (right background) at 10,000 ft. in the Kuh-i-Jupar

P. H. T. BECKETT—PLATE II

5. Fine outwash alluvium by Zangiabad on the plain, crossed by numerous rows of *qanàt* shafts. Bare slopes and scree on limestone outcrops in the middle distance

6. Cultivated land on stony colluvium in a high valley of the Kuh-i-Badaman

7. The head of a *qanàt* shaft in a fallow field of fine outwash alluvium by Ikhtiarab[illegible] the plain. The *qanàt* tunnel had collapsed, and is being lined therefore with earthenware rings (*nars*)

8. Adit of an old *qanàt*

P. H. T. BECKETT—PLATE IV

MAJOR GENETIC SOILS OF THE ARCTIC SLOPE OF ALASKA[1]

J. C. F. TEDROW, J. V. DREW, D. E. HILL, and L. A. DOUGLAS

(Rutgers University, New Jersey, U.S.A.)

Summary

The genetic soils of Arctic Alaska can be arranged in a drainage catena. The mature soils on well-drained sites are Arctic Brown and related soils. The Tundra profile is an imperfectly- to poorly-drained catena member. The Bogs, with permafrost, occupy many of the broad, flat, very wet areas. No evidence of a qualitative soil-forming process unique to the Arctic areas is found. Instead, the Arctic Tundra is primarily a northern extension of the hydromorphic soils of the forested regions, whereas the Arctic Brown and related soils represent the northern extensions of the podzolic process. The term Tundra, when used in connexion with zonal great soil groups along with Podzols, Chernozems, Laterites and related soils, is an erroneous one and its use, except for a hydromorphic soil, should be discouraged. The podzolic process on the stable, well-drained sites weakens northward, resulting in the successive development of Podzols, Minimal Podzols, Arctic Browns, Arctic Browns shallow phase, and, finally, no soil formation.

Introduction

A SOMEWHAT arbitrary line drawn by soil scientists marks the northern extremity of the podzol region in America. North of this line the soils are referred to, at the Great Soil Group level, as Tundra and Bog (with permafrost). Although the soils of the Arctic Tundra of North America are largely unexplored, recent investigations in northern Alaska by the authors indicate the presence of a number of genetic soils in this region. Our first objective was to describe the major genetic soils of the Alaskan Arctic Slope. From these studies it was found possible to offer some hypotheses concerning the soil-forming processes operating in this Arctic environment.

It has been generally implied that the podzolic process gives way to a type of Tundra soil-forming process, the Podzols 'grading' into Tundra soils in the direction of the pole. A climatic optimum exists for podzolization, northward from which the process weakens. The qualitative process of podzolization does not, however, grade into a special type of soil formation unique to the Tundra areas. Instead it grades into one giving rise to soils that are weakly podzolic in character. These have been termed Arctic Brown (Drew and Tedrow, 1957; Tedrow and Hill, 1955) and related soils (Kellogg and Nygard, 1951). Therefore, a second objective—to follow the weakening podzolic process along a theoretical transect from the northern forested areas to the polar deserts—was added to the study.

[1] Journal series paper of the New Jersey Agricultural Experiment Station, Rutgers, the State University of New Jersey, department of soils.

These studies were aided by a contract between the O.N.R., Department of the Navy, and the Arctic Institute of North America. Reproduction in whole or in part permitted for any purpose of the United States Government.

Climate

The climate of northern Alaska is truly Arctic, the mean temperature for July, the warmest month, approximating 50° F., and that of February, the coldest month, approximating −27° F. (Conover, 1953). Precipitation averages 4 to 8 in. a year, with much of it in the form of snow. Relative humidity is very high. The low value for precipitation is somewhat misleading because evaporation is low and moisture may accumulate in the soil directly by condensation. Apparently this condensation does not provide sufficient moisture to cause much leaching in the profile, the effect being primarily that of maintaining the soil in a somewhat more moist state than would be expected in an area of low precipitation. The entire area is underlain by continuous permafrost, the maximum measured thickness near Point Barrow being 1,030 ft. (MacCarthy, 1952).

Soil Conditions

As a result of low soil temperatures and a short growing season, organic matter synthesis and decomposition are very slow. Silt loam textural classes dominate, but considerable variations exist. At one extreme, coarse-textured material is present, as in some of the dune and beach ridge areas of the Arctic Coastal Plain. But the bentonite deposits of the Arctic Foothills consist largely of clay, with only small quantities of silt and fine sand. Soils of the Arctic regions are reported to be predominantly medium-textured, with a large percentage of silt. This suggests the possibility that the rocks and minerals have been weathered mainly through physical processes to silt, at which size-range they reach a somewhat static state, further reduction of size being of only minor significance. Grigorijev (1945), Taber (1943), Tsyplenkin (1946), and others discussed the question of weathering under Arctic conditions, but their findings and opinions are inconclusive. Sigafoos and Hopkins (1952) state that 'grain size of Arctic soils . . . is largely a function of the grain size of parent rock'.

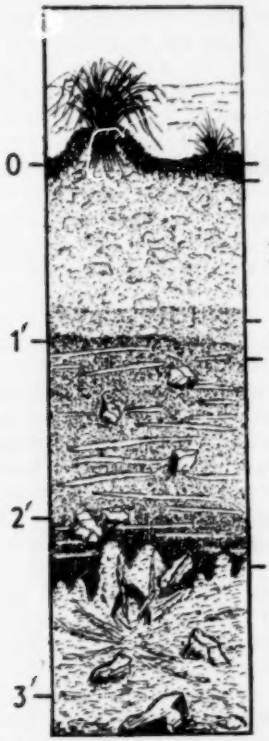
Topography is of major importance in soil formation in the Arctic regions. As the slow seasonal thaw of the active layer progresses considerable water is released. Since the underlying frozen layer in the soil is impervious, drainage water moves sluggishly across and through the active layer. Ridges and narrow watershed divides tend to be better drained than the surrounding flat areas. The latter areas, having little or no runoff, tend to accumulate organic matter and to develop organic soils. Low rates of evaporation, coupled with condensation of atmospheric moisture, contribute to the wet conditions so prevalent in the Tundra (Gorodkov, 1939).

The few descriptions of Tundra soils generally describe conditions only above the frozen layer. In our northern Alaskan investigations mechanical drills and explosives were employed to open up the soil so that the upper portion of the permafrost as well as the active layer could be examined.

Soils of Predominantly Wet Environment

Tundra soils

The most widespread soil of the Arctic Slope of Alaska is the wet mineral soil known as Tundra. This Great Soil Group tends to mantle the undulating and sloping landscape from ridge top to valley bottom,



1. Organic matter, dark brown to black, consisting of partially decomposed sedges, sphagnum, and heaths. This horizon may vary from a thin discontinuous one to an organic mat some six inches thick. Usually very loose, fibrous, wet, and strongly acid.

2. Light olive-brown (2·5Y 5/4) silt loam, usually very wet but, upon drying, is loose and friable. Mottling is nearly always present but in varying degrees. Strongly acid.

3. Dark grey (2·5Y 4/0) silt loam, mottled, very wet. The bottom of this layer approximates to the permafrost table.

4. Very dark grey (2·5Y 3/0) silt loam, permanently frozen. Considerable organic staining in the ice and shreds of organic matter are intermixed throughout the horizon. The bottom of the layer is very uneven and has a much darker colour than the central portion of the horizon. The upper part of the horizon also may have a darker colour than the central portion. The horizon varies from frozen mineral soil to ground ice. Pieces of peaty material are commonly present.

5. Frozen, grey mineral matter interspersed with ground ice. No evidence of organic staining. In many instances the material is virtually clear ice. Weakly acid to calcareous, depending upon parent material.

FIG. 1. Idealized description of a Tundra profile. Soil colours based on field conditions using Munsell colour chips, Munsell Color Co., Baltimore, Md.

and the flat coastal plain areas as well. Silt loam textures predominate. The profiles show little if any textural change among the several horizons that are related to soil-forming processes. Profile characteristics vary in relation to parent material, relief, and time.

Tundra profiles show considerable variation. Local factors, such as the complex pattern of ground ice in the form of ice wedges, veins, lenses, and stems, and the amount and character of the organic material at the surface, leave their marks on the profile morphology. Application of conventional horizon designations in Tundra profiles has little meaning. To avoid misunderstanding, a numerical system is used.

While the idealized Tundra profile is acid in reaction, especially in

the upper horizons, recent field investigations revealed extensive areas of highly calcareous soils in Arctic Alaska. Little is known about the influence of the high calcium content on the soil processes.

Fig. 1 shows an idealized profile thought to typify in general terms the Tundra soils in northern Alaska. Three master horizons are present: (*a*) the active layer (horizons 1, 2, and 3 of Fig. 1), (*b*) the upper portion of the permanently frozen layer (horizon 4), containing considerable organic staining and pieces of organic matter,[1] and (*c*) the permanently frozen parent material without organic staining (horizon 5). The active layer is the only portion of the soil that is subject to seasonal thaw. The appearance of this layer varies at different sites, depending upon such factors as relative wetness, parent material, plant cover, organic matter, and topography. Colours range from yellows and browns, with various intensities of mottling, in the drier areas, to dark greys in the wetter sites. Near the top of the active layer the mottling consists of a spectrum of yellow, orange and grey but the colours near the bottom are darker. The soil is nearly always saturated, and excavations, with few exceptions, fill with water.

The soil-forming process associated with the Tundra profile is primarily one of gleization in a low-temperature environment. There is no evidence to indicate that moisture moves downward into the permafrost. Frost action and solifluction operate simultaneously with soil formation. Frost action tends to disrupt the acquired morphology in some locations. Organic matter is commonly present to depths exceeding several feet. The 'frost churning' discussed in the literature is thought to take place in northern Alaska at an exceedingly slow rate. Cores of finely ground garnet 1 in. in diameter were inserted in a few places to depths approximating 3 ft. After two years no detectable displacement was noted. On the steeper land, however, solifluction processes are active, causing major profile disturbances.

Thickness of the horizons, colour, intensity of mottling, organic-matter content, topographic position, relative wetness, and related criteria were used to separate the Tundra soils into two units. Tentatively, they have been called Upland Tundra and Meadow Tundra. These two units are somewhat analogous in drainage to Low Humic Gley and the Humic Gley soils of the temperate climates. Upland Tundra occupies the relatively drier sites on sloping land and rounded hilltops that afford better drainage than the lower areas. On these Upland Tundra sites the upper horizons tend to show slightly greater oxidation, more brown and yellow coloration, and less organic-matter

[1] The processes by which the organic matter becomes dispersed through the ice in the upper part of the permafrost are unknown. Some possibilities are suggested: (1) Some of the organic matter may have been displaced downward by frost action during a warmer period of the Pleistocene. The dispersion of organic matter and organic staining throughout the ice in this layer indicates that the depth of thaw may have been greater at some time than at present. That there were warmer periods in this region during the past is fairly well established (Grigorijev, 1945). (2) Some of the organic matter may have been translocated slowly downward in the form of a colloidal suspension during a warmer period of the Pleistocene. (3) The present permanently frozen organic stained ice and frozen pieces of peaty material may be profile remnants buried by aeolian and other processes.

accumulation than do those of the Meadow Tundra. Meadow Tundra occupies the lower positions, the flatter areas, and similar situations of poor drainage. Relative wetness of the Meadow Tundra profile is greater, colours are darker grey, the thickness of the surface organic matter is greater, and related conditions of poor drainage increase in intensity, in comparison with the Upland Tundra.

Organic Soils

Wide areas of flat terrain provide little opportunity for surface runoff. The frozen soil layer serves as an impermeable stratum. Under these

1. Reddish brown sphagnum and sedge peat. Fibrous and very wet, usually moderately to strongly acid.

2. Black sphagnum and sedge peat with ice lenses, strongly acid.

3. Frozen black peat and mineral matter with considerable ground ice.

FIG. 2. Idealized profile of a Bog soil formed on a river terrace.

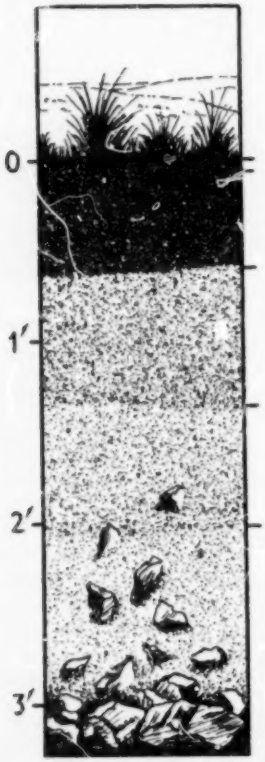
conditions the soils are saturated with water throughout most of the summer months and frequently have water standing on the surface to depths exceeding 1 ft. The waterlogged condition of the soil prevents much organic-matter decomposition, and peaty material tends to accumulate (Fig. 2). Peat thicknesses exceeding 4–6 ft. do not appear to be extensive, but thicknesses exceeding 20 ft. have been observed in isolated cases along swales. The organic soils are usually sedge-sphagnum-grass mixtures, much of the organic material retaining its fibrous condition.

The organic soils are subdivided into Half-Bogs with organic matter accumulations approximately 6 to 12 and, in some instances, 18 in. in thickness, and Bog soils with an organic layer at times exceeding 4 ft.

Because of polygonal development, stream cutting, and related processes, some of the organic deposits are in a comparatively dry environment. The majority, however, remain very wet. On the 'dry' peat areas plant species common to well-drained sites are usually present.

Soils of Predominantly Dry Environment

On escarpments, shoulders, ridges, terrace edges, stabilized dunes, and similar locations, the active layer may have a thickness of as much



A_0. Dark brown to black organic matter.

A_1. Dark brown (7·5YR 3/2) sandy loam with loose single grain to fine crumb structure, moderately to strongly acid.

A_2. Dark yellow-brown (10YR 3/4) sandy loam, moderately to strongly acid.

A_3. Dark yellow-brown (10YR 4/4) sandy loam.

C Very dark grey-brown (2·5Y 3/2) loamy sand, varying from acid to calcareous.

FIG. 3. Idealized profile of an Arctic Brown soil.

as 3 to 5 ft. By virtue of their positions, these sites are well drained. The thickness of the active layer is greater where sand and gravel are present, but well-drained sites of silt loams are found in isolated cases. The mature soil on these well-drained, stable areas has been designated as Arctic Brown (Fig. 3).

The Arctic Brown soil (Drew and Tedrow, 1957; Tedrow and Hill, 1955) is interpreted as a segment of what Russian workers (Filatov, 1945) have designated as dry Tundra in the Siberian Arctic and Subarctic. Where bedrock is within 12 to 18 in. of the surface and drainage is good the Arctic Brown shallow phase (Fig. 4) is commonly present. Shallow,

0
1′
2′
3′
A$_0$. Dark brown to black organic matter.
A$_1$. Dark brown (7·5YR 3/2) sandy loam with loose single grain to fine crumb structure.
A$_2$. Dark yellow-brown (10YR 3/4) sandy loam.
C. Very dark grey-brown (2·5Y 3/2) loamy sand.
D. Bedrock.

FIG. 4. Arctic Brown soil, shallow phase.

well-drained soils are more likely to be found in the higher elevations in the Southern Arctic Foothills, but they have also been observed on unconsolidated deposits as far north as the coastal areas.

Some of the soils are gradational between the Arctic Brown and Tundra. They tend to have most of the features of the Arctic Brown, especially in the upper horizons, but the lower horizons have a gley appearance at a depth of 12–24 in. Permafrost is nearer the surface than in the typical Arctic Brown soil, being usually 18 to 30 in. deep. The drainage of this soil is somewhat analogous to that of a 'moderately well-drained' soil of the temperate climates. An interesting feature of these soils is the presence of a black organic colour immediately above

the permafrost. This appears to result from the slow, downward migration of the organic matter which, on reaching the bottom of the active layer, becomes trapped immediately above the permafrost. This soil is referred to as Arctic Brown moderately well-drained phase.

The Arctic Brown profiles can, therefore, be subdivided into Arctic Brown normal phase, Arctic Brown shallow phase, and Arctic Brown moderately well-drained phase.

Lithosols

The rugged terrain of the mountains is characterized primarily by rock land, generally with no soil cover but occasionally covered with shallow 'dry' soil having a brown surface horizon that may attain a thickness of 1–6 in. Topography is so steep and erosion so rapid that the soil-forming processes cannot keep pace with processes of mass wasting.

Regosols

Certain alluvial, aeolian, marine, outwash, and talus deposits are well drained to depths exceeding 2 to 3 ft. Because of the youthfulness of the area, many of the soils of these sites have developed little or no semblance of a genetic profile. Permafrost is unusually deep, often as much as 4 to 6 ft. These areas have been included with the Regosols.

Schematic Arrangement of the Genetic Soils

A drainage sequence of profiles in the Arctic regions has long been broadly implied by many investigators. Filatov (1945) recognized a dry Tundra associated with sandy or stony, coarse soils with a dry turfy layer and many kinds of Tundras with impeded drainage. Sheludyakova (1938) describes Lichen Tundra formed under good drainage conditions, grassy cotton-grass Tundras formed under poor drainage, and marshy lake-plain littoral Tundra formed in the wet Tundra marshes. Dansereau (1954) implies drainage sequences in Baffinland, and information and samples furnished by him indicate the presence of drainage sequences. Smith (1956) describes a series of soils in Spitzbergen which falls into a drainage catena. Retzer (1956) recently described a somewhat similar drainage sequence in the Alpine Tundra regions of the Rocky Mountains.

The major soil profiles of the Alaskan Arctic Slope can be arranged in the form of a drainage catena, the Arctic Brown representing the mature, well-drained soil of the region (Fig. 5). In grading from the deep, well-drained to shallow, well-drained condition, there is no change in the type of soil-forming processes, but only a diminution of profile thickness. In the shallow soils the A_3 horizon is no longer evident. Continuing through more shallow conditions, the A_1 horizon maintains about the same thickness, but there is a marked decrease in the thickness of the A_2. With very shallow soils only dry organic matter overlying coarse matter is evident. Finally a point is reached where there are no acquired soil features, only scattered crustose lichens over rock or rock debris. The shallow Arctic Brown profile is commonly present at higher altitudes and elevations where bedrock is near the surface as well as

under the more severe Arctic climates where the rate of soil formation is exceedingly slow. The shallow Arctic Brown profile is also present on the more recent deposits, the shallowness of the profile being due to insufficient time having elapsed for a deep profile to develop.

In grading from the Arctic Brown normal phase to the moderately well-drained phase (Fig. 5), permafrost is present at depths approximating 18 to 30 in., and a gley appearance is apparent 1 to 6 in. immediately

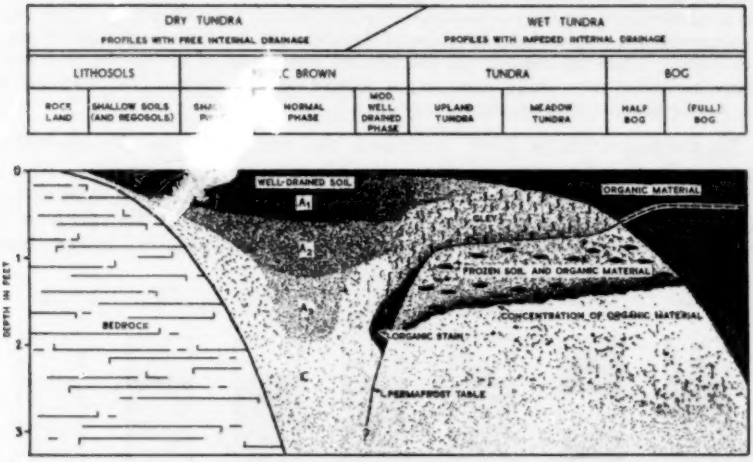


FIG. 5. Major genetic (drainage) sequences in the soils of the Arctic Slope of Alaska (diagrammatic).

above the permafrost table. Where the permafrost table occurs near the surface, the gley appearance is intensified, and the Tundra profile becomes evident. Complete saturation of the profile gives rise to organic-matter accumulation and the formation of Bog soils.

Fig. 5 diagrams the four major soils—Lithosols, Arctic Brown, Tundra, and Bog. The mature or zonal soil is considered the Arctic Brown, while the Tundra and Bog soils are definitely considered intrazonal soils.

Podzolic Process in the Arctic Environment

Statements and inferences that the podzolic process 'grades' into a completely different soil-forming process in Arctic regions as one proceeds northward are without foundation. The vast wet expanses of the Arctic are primarily Tundra soils, but they are forming under a wet environment and cannot be thought of in terms of mature soils such as Podzols and Chernozems. The concept that the Tundra process is qualitatively inseparable from the gley process has been carefully analysed and presented by Gorodkov (1939), a seasoned Arctic pedologist, who states:

The differences between the gleyey and podzolic-gleyey soils of the northern

forest zone and the Tundra and polar-desert soils is not qualitative but quantitative. . . . Only Liverovskii tries to find special soil-forming processes in the Arctic, and he sometimes classifies the soils as 'a special variant of the gley-marsh processes' sometimes as 'a special type of soils of the gleyey-marshy series'. In confirming his opinion, he draws on data from Zaitsev and Afanas'ev which is analogous to his own, forgetting both their works relate to soils of the forest zone, and not to the Arctic. Therefore his reference to them merely confirms the lack of special Arctic soil formation. . . . Such (Tundra) soils are commonly included in the classification schemes along with Podzols, Marshy-gleyey, Chernozem, and others although there are no serious foundations in principle or in fact for such a classification. There was some excuse for a special classification of Tundra soils in Dokuchaev's and Sibertsev's time, when information on the natural conditions of the tundra zone was scarce and often completely incorrect; at present we have no basis for considering the Arctic as something special by way of soils.

Numerous workers have described the weakening of the podzolic process in the direction of the pole (Filatov, 1945; Gorodkov, 1939; Meinardus, 1930; Sheludyakova, 1938; Sochava, 1933). This weakening of the process is due primarily to climatic conditions in that there is a smaller amount of total precipitation and temperatures are lower than

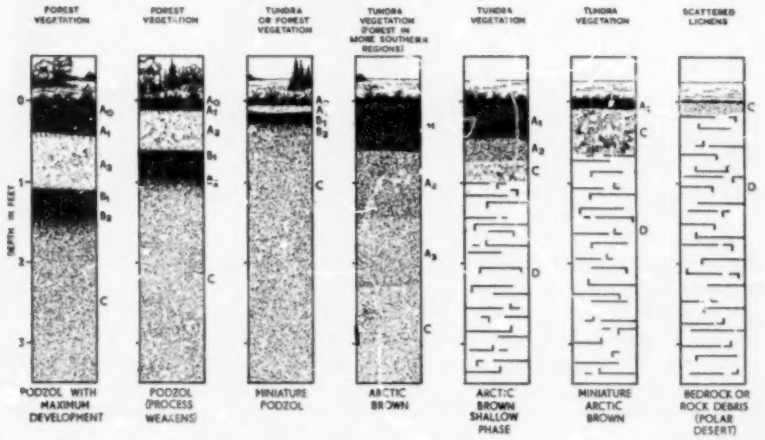


FIG. 6. Suggested mature profile sequences from the zone of maximum podzolization (*left*) northward to the zone of polar deserts (*right*).

farther south in the well-defined Podzol areas. Biologic activity and chemical weathering are weak in the far-north areas. Traces of mineral elements brought into solution in the northernmost regions move downward in barely measurable quantities. In some cases no downward movement is apparent. If the summer precipitation were greater in the areas of Arctic Brown soil and if the soils had sufficient permeability and drainage, Podzols would probably dominate the well-drained sites. The degree of this podzolic development would be in proportion to the increase in rainfall.

The diagrammatic presentation commonly employed to show the relation of great soil groups to climate indicates that Tundra soils form under conditions varying from 'dry-cold' to 'wet-cold'. This concept can be quite misleading because Tundra soils in Alaska form under conditions of high humidity but low precipitation. During the summer months relative humidity seldom drops below 70–80, and most of the time it exceeds 90 per cent. On the other hand, precipitation in the Arctic is very limited and leaching potential is correspondingly low.

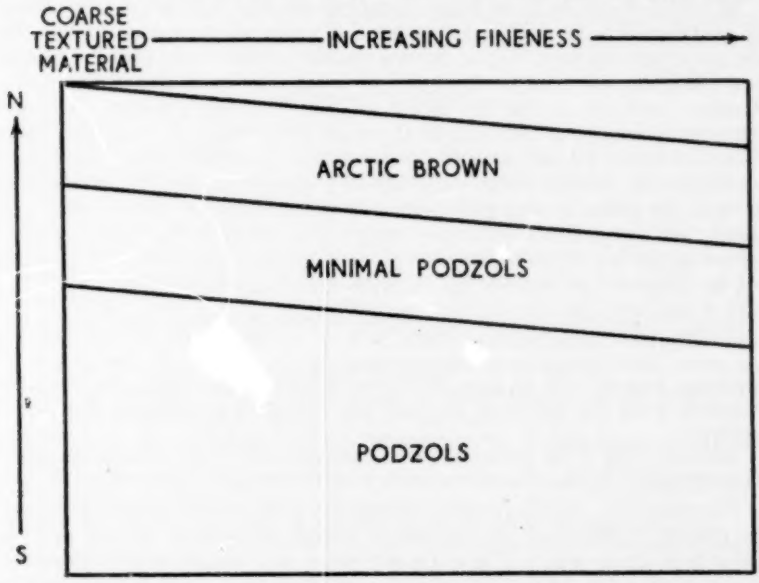


FIG. 7. Influence of textural composition on the degree of podzolization of the well-drained sites at northern latitudes.

The change from the Podzols to the brown surface soils of the Arctic and Subarctic regions is one of gradual transition. The qualitative process expresses itself in varying intensities that tend to diminish northward. The results of the varying intensities of podzolization are idealized in a sequence of profiles in Fig. 6. Considerable interfingering of Arctic Brown and Minimal Podzol profiles occurs, depending upon the nature of the parent material (Fig. 7), age, relief, altitudinal limits, and related factors. Signs of a feeble podzolic process are manifested in Arctic Brown, Subarctic Brown Forest, and related profiles. Kellogg and Nygard (1951) regard what is designated as Subarctic Brown Forest soil of Central Alaska as representing a stage of immaturity before Podzol. This concept has merit and the nomenclature is one of semantics. A very weak podzolic process is operating in the area but at an exceedingly slow rate. If the process operated on a stable land surface for very long periods of time a soil with distinct Podzol features could possibly develop.

The brown surface soils are present, however, on many kinds of material of diverse ages, and they appear to be in reasonably good equilibrium with their environment. If the Subarctic Brown Forest soil is considered transitory, then the Grey-Brown Podzolic, Brown Podzolic, and related soils are likewise transitory and, in time, will develop into Podzols. If the Grey-Brown Podzolic, Brown Podzolic, and related soils are considered mature, then the Subarctic Brown Forest and Arctic Brown soils are also mature, regional soils.

Minimal Podzols have been detected on the sandy Coastal Plain of northern Alaska within a few tens of miles of the Arctic Ocean. In the same general areas Arctic Brown profiles without any visible signs of podzolization are found. Podzol formation has been reported by the Russian workers on the dry sands of the Siberian Tundra. Sochava (1933), reporting on the Anabar drainage basin west of the lower Lena River, states: 'One may almost always detect a podzol-formation process on the sands and subsands.' Gorodkov (1939) describes the weakening of both the podzolic and gley processes in the direction of the pole. He states that the podzolic process weakens first, whereas the gleys are preserved up to the extreme limits of the land that is free of ice. In discussing the podzolic process in the Tundra area Gorodkov states:

> In the Gydan tundra we observed not only podzolized spots and interlayers in the sands under the lichen and moss-lichen cover as far north as the 71st parallel but also some manifestation of an accumulation horizon. Liverovskii describes well-developed podzolic soils on sands of the Bol'shezemelskaya tundra. On the Kola Peninsula up to the very coast one may find podzols, but with a weak podzolic horizon.
>
> The weakening of the podzolic process eastward leads to the fact that generally we do not find podzolic soils even in sandy grounds in the tundra zone of the far east.

Theoretically, as one proceeds northward, on similar parent material the Arctic Brown soil grades into a weakly developed profile until a point is reached where it is quite primitive and the developed features of the profile consist mainly of a brown surface 1 to 2 in. in thickness. Finally, a climatic condition is reached where on dry sites sparse dry lichens do not produce any discernible changes in the parent material, and there is no evidence of soil. This condition corresponds to the polar deserts described by Russian workers (Gorodkov, 1939).

The weakening podzolic process in a northerly direction is well illustrated by Gorodkov's map showing a northern zone adjoining the Arctic Ocean in Siberia with soils having *scarcely perceptible podzolic features*. To the south of this zone is a second zone of *weakly podzolic features* and farther to the south a third zone of *podzolic soils*. This principle has been described by other Russian investigators. Gorodkov states that 'the difference between the gleyey and podzolic-gleyey soils of the northern forest zone (Siberia) and the tundra and polar desert soils is not qualitative but quantitative. They lead only to varied intensity of the podzolic and gleyey process.'

The misconceptions about the soils of the Tundra are largely a result of a confusion of processes of soil formation with areal distribution. In

proceeding from the Podzol zone to the Arctic regions the podzolic process continues to operate on well-drained sites, but with a marked decrease in intensity. In the far northern Arctic regions the podzolic process is near the zero point, representing only a potential.

Northward from the forested areas the proportion of well-drained soils diminishes greatly (excluding the areas where consolidated bedrock is at or near the surface). The deep, well-drained soils of the north give way to an overwhelming increase in poorly drained land. The major factors causing this great shift to poorly drained soils include: presence of permafrost, low evaporation, low temperatures, and poorly developed drainage patterns.

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OBSERVATIONS ON THE PEDOLOGY AND FERTILITY OF SOME KRASNOZEMS IN NORTHERN NEW SOUTH WALES

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Summary

Eight krasnozem (red-earth) profiles representing a wide range of environments have been studied. Contrasting features of the soils can be explained by differences in parent material, climate, vegetation, and land use. The main effects corresponding to these variations are seen in the relative contents of total and readily soluble aluminium, organic carbon, nitrogen, organic phosphorus, and of exchangeable metal cations.

Land utilization appears to have led to losses in organic carbon, nitrogen, organic phosphorus, exchangeable cations, and 'available' manganese. These losses suggest the possibility of a potassium deficiency and are in agreement with observed nitrogen deficiencies.

The cation-exchange capacity of the organic matter is much greater than that of the inorganic matter, and in some soils extrapolation suggests that losses of organic matter threaten the capacity of the soils to retain cations.

I. *Introduction*

KRASNOZEMS (Russian, *krasnaya zemlya* = red earth) in Eastern Australia have attracted attention within recent years because of an alleged decline in their fertility and of difficulty in explaining their genesis. This paper presents some observations concerning the pedology and fertility of some contrasting members of this soil group that were made during a study of the solubility and retention of phosphate (Colwell, 1955).

To cover a wide range of pedological environments, virgin profiles were selected representing the predominant krasnozem soil types of the Ben Lomond, Dorrigo, Wollongbar, Glen Innes, and Inverell districts. In the first three areas it was also possible to obtain corresponding cultivated profiles to assess the effects of agricultural development.

II. *Field Description of the Soils*

The soil was examined and sampled to a depth of 3 ft. at each site and, by means of auger borings, deeper horizons were examined to a total depth of 6 ft. Because of the absence of marked variations in the profiles, the samples were taken from the arbitrary depths of 0–3, 3–6, 6–9, 9–12, 12–18, 18–24, and 24–36 in., except with the Dorrigo virgin profile, where, because of the presence of a basalt floater,[2] the deepest sample was from 18 to 25 in.

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[2] A basalt 'floater' is a stone, boulder, or band of unweathered basalt which is likely to be found 'suspended' at any depth in the krasnozem profile.

Profile descriptions

Ben Lomond, profile 1v. Virgin, uncleared open savannah woodland of *Eucalyptus viminalis* subjected to occasional light grazing by travelling stock, mid-slope, gradient 4–5°, elevation 4,680 ft., basalt parent material, 2 miles east of Ben Lomond.

0–6 in. Dark reddish-brown light clay, well-developed fine crumb structure, grading into 6–24 in. brownish-red medium clay, crumb structure becoming coarser with depth, grading into 24–48 in. red medium clay, nutty structure becoming finer with depth, 48–72 in. yellowish-red gritty clay, very fine crumb structure, small iron-manganese concretions becoming very abundant with depth.

Profile 1c. Old cultivation paddock, cropped continuously to maize and potatoes for 42 years prior to sampling, with no addition of fertilizer, mid-slope, gradient 4–5°, elevation 4,660 ft., basalt parent material, 200 yards from profile 1v.

0–6 in. Brown light clay, powdery structure, grading into 6–12 in. red-brown light clay, poor crumb structure, grading into 12–23 in. light red-brown light clay, crumb structure becoming coarser with depth, grading into 23–40 in. light red medium clay, nutty structure grading into 40–72 in. yellowish-red medium clay, fine crumb structure, small iron-manganese concretions becoming very abundant.

Dorrigo, profile 2v. Virgin, uncleared rain-forest, mid-slope, gradient 2°, elevation 4,000 ft., basalt parent material, 'Mountain Top', Dorrigo.

0–9 in. Brown loam, strongly developed very fine crumb structure, grading into 9–25 in. brownish-red clay loam, becoming heavier to light clay with depth, crumb structure. Below 25 in. fresh unweathered basalt 'floater'.

Profile 2c. Old cultivation paddock, cropped to maize continuously from 1920 to 1940 with no fertilizer, and paspalum pasture, grazed with dairy cattle to time of sampling in 1952, mid-slope, gradient 4°, elevation 4,100 ft., basalt parent material.

0–6 in. Greyish-brown loam, strongly developed fine crumb structure merging into 6–12 in. red-brown loam, crumb structure, merging into 12–40 in. brownish-red light clay, crumb structure, merging into 40–72 in. red light clay, crumb structure.

Wollongbar, profile 3v. Virgin uncleared rain-forest, in Rous Nature Reserve, on flat-topped hill, gradient 0° 30′, elevation 500 ft., parent material basalt.

0–10 in. Reddish-brown loam, strongly developed very fine crumb structure, merging into 10–72 in. red clay loam, becoming heavier to light clay with depth, crumb structure, occasional stones.

Profile 3c. Old cultivation paddock, cropped continuously from about 1890 to 1930 with no fertilizer, paspalum pasture, grazed with dairy cattle up to time of sampling in 1952, on flat-topped hill, gradient 0° 30′, elevation 540 ft., parent material basalt, 8½ miles east of Lismore.

0–9 in. Reddish-brown loam, strongly developed fine crumb structure, merging into 9–72 in. red clay loam becoming somewhat heavier to light clay with depth, occasional stones.

Glen Innes, profile 4v. Virgin uncleared land, open savannah woodland of *Eucalyptus albens*, crest of ridge, elevation 3,520 ft., parent material relic laterite (Pleistocene) developed in turn from Tertiary basalt. 2 miles south of Glen Innes.

0–5 in. Red-brown gritty loam, very fine crumb structure, merging into 5–10 in. red gritty loam, crumb structure, merging into 10–24 in. red clay loam, crumb structure, merging into 24–36 in. red very gritty clay loam containing particles of decomposing laterite.

Inverell, profile 5v. Virgin uncleared land, sparsely populated woodland, of ironbark (*E. crebra*) and *Acacia* spp. near crest of hill, slope 2–3°, elevation 2,000 ft., parent material relic laterite (Pliocene?) derived in turn from Tertiary basalt.

0–6 in. Dark red-brown loam, very powdery, 'snuffy' structure, merging into 6–15 in. red-brown loam, powdery structure, grading into 15–94 in. red loam, powdery structure, occasional laterite concretions.

III. *The Pedological Environment*

The available climatic data for the five districts are summarized in Table 1 and show a considerable range of temperature and rainfall.

TABLE 1

Meteorological Data from Localities near Sampling Sites

Locality	*Mean temp. (°F.)*		*Mean rainfall (in.)*
	Max.	*Min.*	
Ben Lomond . . .	65*	41*	38
Dorrigo . . .	..	..	74
Wollongbar . . .	78†	55†	66†
Glen Innes . . .	68	44	31
Inverell . . .	75	45	30

* Temperatures are those for Guyra.
† Rainfall and temperature figures are those for Alstonville and Lismore respectively.

The underlying rock in each case is basalt. The basalts of the five districts are very similar, fine grained, and probably belong to the same general extrusion period of early to mid-Tertiary times (Voisey, 1945; Owen, 1949).

The Glen Innes and Inverell krasnozems are not derived directly from basalt but from an underlying fossil laterite formation which has in turn been derived from basalt. Alternative views are that they constitute an upper horizon of the original laterite profile or are relict soils of the same age as the laterite. But in view of their topographic situations on the crests of small hills and their relatively high susceptibility to erosion under present-day conditions, these latter theories seem unlikely. It is difficult to understand how they could have persisted from Miocene-Pliocene times, through arid and pluvial cycles, to the present day. Moreover, in the case of the Glen Innes soil the gradation at a

depth of about 3 ft. into decomposing laterite is clear evidence of the laterite being the parent material. Because of the great depth (greater than 10 ft.) of the Inverell soil, the underlying parent material was not encountered, but laterite is clearly indicated by outcrops on the surrounding slopes below the level of the krasnozem. Because in these soils the laterite is the actual parent material, they are referred to as krasnozems, rather than 'lateritic krasnozems' (Stephens, 1953) which they closely resemble in morphology.

The virgin vegetation varies considerably from dense rain-forests in the Wollongbar and Dorrigo districts to open savannah woodlands of *Eucalyptus viminalis* and *E. albens* in the Ben Lomond and Glen Innes districts and to the sparsely populated woodland of iron-bark (*E. crebra*) in the Inverell district. These differences are expressions of the differences in climate and, in the case of the Inverell krasnozem, of a low soil fertility. The differences between the virgin and cultivated soils are, however, largely a direct consequence of a change in vegetation. With continuous cultivation, the soils in all these districts become lighter in colour, lose their fine crumb structure, and become powdery and susceptible to erosion. The structure is maintained under well-managed pasture, but in the Wollongbar and Dorrigo districts the colour is still lighter than in the few remaining areas of virgin forest available for comparison.

The effects of topography have not been studied in this investigation, but other work (Nickolls *et al.*, 1953; Hallsworth *et al.*, 1952) has shown that it has very little effect on the profile morphology of the Wollongbar and Dorrigo krasnozems, whereas in the Ben Lomond district there are variations from shallow red-brown clay loams at the top of the slopes to deeper, darker, and heavier soils, often with a mottled B horizon, at the bottom of the slopes.

IV. *The Constitution of the Soils*

1. *Total analysis*

Total Fe, Al, Si, Ti, Mn, and P have been determined on a selection of samples from the profiles by sodium-carbonate fusion, organic carbon by the Walkley-Black method, and total nitrogen by a Kjeldahl semi-micro method. Some results are given in Tables 2 and 3 and full analytical data may be obtained from the author.

The soils are all highly sesquioxidic, but, whereas the high total iron and titanium content appears to be fairly uniform throughout the whole group of soils (ranges of 18 to 29 per cent. Fe_2O_3 and 3 to 7 per cent. TiO_2), there are clear differences in both total aluminium and manganese (ranges of 6·6 to 31 per cent. Al_2O_3 and 0·04 to 0·94 per cent. Mn_3O_4). Silica content shows a general inverse relationship to the sesquioxides, particularly the alumina. Compared with the other soils, the Glen Innes and Ben Lomond profiles (4v, 1v, 1c) have clearly much lower overall aluminium contents (6·6 to 19 per cent. Al_2O_3), higher total manganese contents (0·52 to 0·94 per cent. Mn_3O_4), and, considered as a whole, are less sesquioxidic.

The organic-carbon and nitrogen figures are, in general, high. As would be expected, both constituents decrease with depth down the profiles, but even for the 2–3 ft. sample the amounts in most instances are still appreciable, ranging from 0·3 to 3·1 per cent. organic C. Comparing the virgin soils, the Dorrigo profile, 3v, contains the greatest amounts of organic carbon and nitrogen, and the amounts of both are progressively smaller for the Wollongbar, Ben Lomond, Glen Innes, and Inverell profiles, following the order of decreasing rainfall.

The virgin soil, in each case, contains more organic carbon and nitrogen than the corresponding cultivated soil. The differences seem to be a direct consequence of exploitative land use over the past 50–100 years. It is particularly noteworthy that the differences in nitrogen contents for the Dorrigo and Wollongbar pairs are relatively much greater than the corresponding differences in organic carbon. In the case of the cultivated Wollongbar soil, 3c, there is the very striking contrast that whereas 23 years under grass following a period of intensive cultivation has apparently raised the organic-matter content to about the same level as in the virgin soil, there is still a big difference in nitrogen content.

TABLE 2

Total Iron, Aluminium, and Manganese, 'Free Iron and Aluminium', and 'Available' Manganese in Surface (0–3 in.) Samples

Soil	*Total* Fe_2O_3 (%)	*Free* Fe_2O_3 (%)	*Total* Al_2O_3 (%)	*Free* Al_2O_3 (%)	*Total* Mn_3O_4 (%)	*Available* Mn_3O_4 (%)
Ben Lomond: virgin	18·2	14·2	16·0	2·4	0·82	0·25
cultivated	26·1	18·1	11·3	3·0	1·13	0·19
Dorrigo: virgin	20·7	14·9	21·2	4·5	0·15	0·03
cultivated	19·5	16 8	26·7	4·7	0·13	0·02
Wollongbar: virgin	27·4	21·4	25·4	5·7	0·37	0·11
cultivated	22·9	19·5	23·8	4·6	0·19	0·04
Glen Innes: virgin	25·7	22·2	6·6	1·4	0·94	0·29
Inverell: virgin	23·9	20·0	24·5	5·4	0·14	0·01

TABLE 3

Organic Carbon (Walkley–Black), Total Nitrogen, Total Phosphate, and Organic Phosphate Contents in Surface (0–3 in.) Samples

Soil	*Organic* C (%)	*Total* N (%)	*Total* P_2O_5 (%)	*Organic* P_2O_5 (%)
Ben Lomond: virgin	5·0	0·37	0·51	0·155
cultivated	2·5	0·18	0·63	0·108
Dorrigo: virgin	7·9	0·81	0·77	0·218
cultivated	5·4	0·41	0·72	0·170
Wollongbar: virgin	5·8	0·62	1·10	0·238
cultivated	5·4	0·43	0·54	0·164
Glen Innes: virgin	4·0	0·28	0·93	0·093
Inverell: virgin	4·6	0·32	0·30	0·036

The total-phosphate levels are, in general, very high. Of the eight profiles the Inverell profile, 5v, has the lowest phosphate content (0·12–0·34 per cent.) and the Wollongbar profile, 3v, the highest content (0·92–1·10 per cent.).

2. *Organic phosphorus*

The organic phosphorus in the surface samples was estimated by the hot 0·1 N HCl—cold 0·1 N NaOH extraction method of Saunders and Williams (1955) (see Table 3). The method depends on alkaline extraction of the organic phosphorus after acid pre-treatment of the soil to remove bases. The organic phosphorus is then estimated by difference between the total and inorganic phosphorus in the extracts. Apart from the disadvantage that the value in this type of method is obtained by difference, organic-phosphorus estimates are subject to many uncertainties such as incomplete extraction and hydrolysis of the organic phosphorus (Black and Goring, 1953). Nevertheless, the extraction values can be accepted as valid estimates of the general levels of organic phosphorus in the soils.

The organic phosphorus accounts for 10–35 per cent. of the total phosphorus and except for the Inverell sample the general level is high. The figures show the same general trends as for organic matter. In particular, the organic-phosphorus content decreases with decreasing rainfall and is considerably lower in the cultivated than in the virgin soils.

With one exception, the organic-carbon/organic-phosphorus ratio is appreciably less than 200, the limit below which microbial decomposition of the organic matter can be expected to cause an initial mineralization of the organic-phosphorus compounds (Black and Goring, 1953). The Inverell sample, 5v–1, has a much wider ratio which could indicate a tendency towards immobilization of inorganic phosphate by microbial activity. There is no consistent difference between the cultivated and virgin soils.

3. '*Free iron and aluminium*'

Estimations of the 'free iron' and 'free aluminium' in the surface samples were made using a modification of the sodium-hydrosulphite extraction procedure of Mackenzie (1954). This consisted essentially of four alternate extractions of 0·2 g. 100-mesh soil with sodium hydrosulphite and 0·05 N HCl. This procedure gave an adequately complete removal of 'free iron oxides', as judged by the change in colour and the fairly definite end-point in the iron contents of the successive extracts. Since there was also a fairly sharp end-point to the aluminium removed in successive extractions the method also seems to extract a fairly well-defined category of 'free alumina'.

The outstanding feature of the 'free iron-oxide' values (Table 2) is that they are very high and represent from 69 to 86 per cent. of the total iron. By comparison, the aluminium values are much lower and account for only about 20 per cent. of the total.

As with the total contents, the 'free aluminium' shows much larger relative variations than does iron, the Glen Innes and Ben Lomond samples giving appreciably lower values than the other soils.

TABLE 4

Exchangeable Cations, expressed as m.e. per 100 g. Soil, and pH. (Full data for these profiles may be obtained from the author.)

Soil	*Depth (in.)*	Ca	Mg	K	Na	H	pH
Ben Lomond: virgin	0–3	13·00	2·05	1·18	0·13	11·6	6·0
	24–36	4·98	1·21	0·58	0·13	4·3	6·1
cultivated	0–3	8·74	1·09	0·19	0·27	11·6	5·9
	24–36	3·24	1·76	0·20	0·10	3·8	5·7
Dorrigo: virgin	0–3	6·27	0·79	0·80	0·15	23·9	5·4
	18–24	1·15	0·22	0·31	0·45	14·7	4·8
cultivated	0–3	2·08	0·32	0·78	0·14	17·8	5·3
	24–3	0·16	0·07	0·35	0·07	5·3	5·5
Wollongbar: virgin	0–3	7·77	1·10	0·83	0·19	14·8	5·9
	24–36	1·28	0·32	0·44	0·13	6·4	5·3
cultivated	0–3	4·38	0·64	0·28	0·18	13·3	5·6
	24–36	4·57	0·13	0·15	0·13	2·6	6·8
Glen Innes: virgin	0–3	13·10	1·38	1·66	0·28	9·4	6·1
	24–36	5·79	1·63	1·76	0·09	2·1	7·4
Inverell: virgin	0–3	11·10	1·28	1·96	0·09	9·0	6·7
	24–36	0·47	0·98	0·65	0·06	4·2	5·8

4. *'Available' manganese*

The 'available' manganese in the surface soil samples was determined by the 0·5 per cent. hydroquinone extraction procedure of Jones and Leeper (1951*a*, *b*). Comparison of corresponding virgin and cultivated samples (Table 2) shows that the 'available' manganese, both the absolute amount and the proportion of the total, is lower in the cultivated soils. This suggests a preferential removal and loss of the more available fraction of manganese following the agricultural development of the soils.

5. *Exchangeable cations*

Exchangeable cations were extracted with normal ammonium acetate (pH 7·0) and exchangeable hydrogen was estimated by leaching with normal barium acetate (pH 7·0) and titrating the leachate to pH 7·0 with barium hydroxide.

The exchange complex in each profile is unsaturated (Table 4). The levels of metal cations show marked decreases with depth and, comparing the different districts, there is a general tendency to decrease with increasing rainfall. In each case, the level is higher in the virgin than in the cultivated profile. These trends illustrate the general effect of increased leaching with increasing rainfall, the enrichment of the

surface horizons by leaf litter and the exploitative effects of land development.

The most abundant metal cation is calcium, varying from 10 to 13 m.e. per 100 g. at the surface for the drier districts to very low values of the

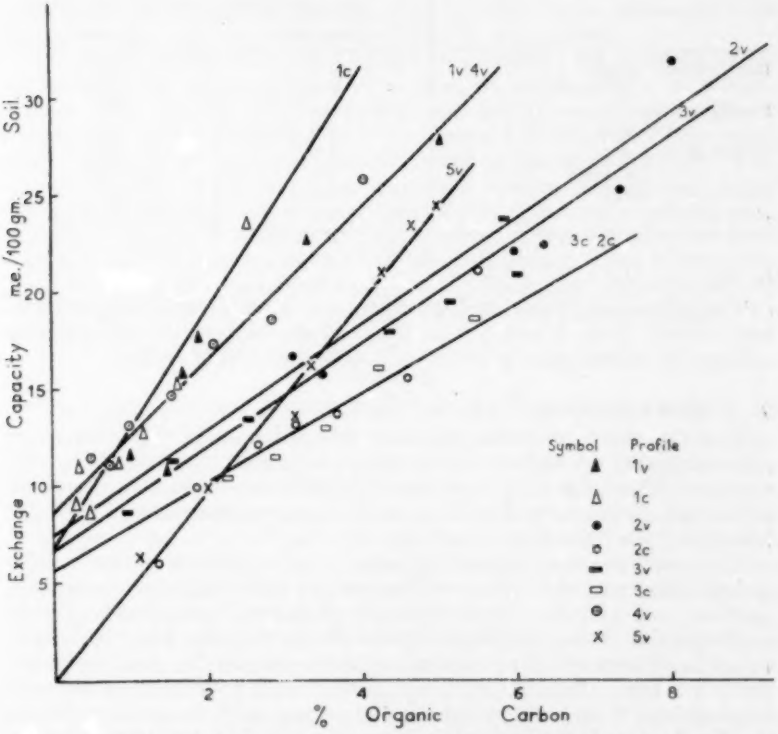

Fig. 1. Relationship between organic-carbon content of individual profiles and exchange capacity. Extrapolation to 0 per cent. carbon shows very low exchange capacity of the inorganic exchange complex.

order of 1 m.e. at depths greater than about 12 in. in the wetter districts. The magnesium values are much smaller (2·05–0·07 m.e.), while the potassium values (1·96–0·15 m.e.) and sodium values (0·45–0·06 m.e.) are very low.

Within each profile, the exchange capacity, estimated by summation of the exchangeable cations, shows a close linear relationship to the organic-carbon contents (Fig. 1). By extrapolation an estimate can be made of the exchange capacity of the inorganic portion, and, by difference, the organic portion of the soil. These values are given in Table 5. They demonstrate that the greater part of the cation-exchange complex in the surface horizons is provided by the organic matter.

TABLE 5

Exchange Capacity of Inorganic and Organic Fractions of the Soil, estimated by Extrapolation of Fig. 1

Soil	Exchange capacity (m.e. per 100 g.)	
	Inorganic	*Organic*
Ben Lomond: virgin	8·6	400
cultivated	6·8	630
Dorrigo: virgin	7·5	280
cultivated	5·6	234
Wollongbar: virgin	6·6	280
cultivated	5·6	234
Glen Innes: virgin	8·6	400
Inverell: virgin	0·0	490

6. *pH*

The pH values (Table 4) obtained from 1:2·5 soil: water suspensions, vary widely from about 7·0 in the samples richest in exchangeable cations, to values under 5 in the soils most depleted of cations.

7. *Mineral constitution of the clay fraction*

The clay fractions (2μ e.s.d.) from selected samples were examined mineralogically by differential thermal analysis (d.t.a.) and X-ray diffraction. The d.t.a. technique and apparatus used was that described by Mackenzie (1952*a*). The X-ray studies were carried out by Mr. W. A. Mitchell at the Macaulay Institute.

The predominant minerals present are a mineral of the kaolin group, illite, and the iron- and aluminium-oxide minerals haematite, goethite, and gibbsite. Small amounts of quartz, lepidocrocite, ferric-oxide gel (or cold-precipitated hydrated ferric oxide, see Mackenzie, 1952*b*), and vermiculite or chlorite occur in some of the profiles. From the 'slope ratio' (Bramão *et al.*, 1952) the kaolin appears to be the disordered form frequently found in fireclays and in some instances, as in the Ben Lomond profiles, halloysite may occur. The haematite in every instance gave a very diffuse X-ray diffraction pattern, indicating a very fine state of subdivision. The presence of amorphous material may be indicated by the fact that, where both X-ray and d.t.a. data were available, the total minerals estimated were mostly in the 75–95 per cent. region. This deficit may also of course be attributed to the limited accuracy of some of the determinations, which in most instances could be made only to the nearest 5 per cent.

The mineral assemblages of the clay fractions are characteristic for the profiles from the different districts.

For the Ben Lomond profiles the dominant constituents are disordered kaolin (40–65 per cent.) and illite (10–15 per cent.), with small amounts of haematite and traces of gibbsite, goethite, and ferric-oxide gel. The ferric-oxide gel is not present in any other profile and its occurrence suggests that in this instance the considerable deficit shown

by the total of the minerals is due to the presence of amorphous material.

The Glen Innes profile is similar in composition to the Ben Lomond profiles, with relatively large amounts of kaolin (35–40 per cent.) and illite (5 and 25 per cent.), but it differs in the presence of large amounts of haematite in the deepest sample. There is 5 per cent. lepidocrocite in the surface sample, but little or no gibbsite or goethite.

The profiles representing the Dorrigo, Wollongbar, and Inverell krasnozems have, by comparison, a clay fraction much richer in sesquioxides. The Dorrigo profiles contain the largest amounts of gibbsite (35–40 per cent.), moderate to large amounts of illite and haematite, and comparatively small amounts of slightly disordered kaolin. The Inverell profile is similar, with somewhat smaller, though still large, amounts of gibbsite, and differs mainly by the presence of 10 per cent. lepidocrocite at the surface and an appreciable amount of amorphous material, as indicated by the total of the constituents. The Wollongbar profiles are similar with large amounts of gibbsite and differ mainly by containing somewhat large amounts of disordered kaolin and moderate amounts of goethite (5–15 per cent.).

Discussion

The eight profiles described in this paper all possess features of morphology (colour, texture, structure) and chemical composition (high sesquioxide content, depleted base status) that qualify them for classification as krasnozems, as defined by Leeper (1948) and Stephens (1953). This study demonstrates the wide variations that can occur within this broad grouping. Apart from such variations as total and 'free' iron, and total titanium, that appear to have little pedological significance, the profiles show contrasting features which reflect variations in climate, parent material, and land use (vegetation).

The effects of climate are seen in the general increase of organic carbon, nitrogen, and organic phosphorus content, and the general decrease of exchangeable metal cations, with increasing rainfall. Also, comparing the Ben Lomond, Dorrigo, and Wollongbar profiles, which have the same parent material, the higher silica and much lower aluminium contents of the Ben Lomond profiles indicate less severe weathering attributable to the lower rainfall.

Parent material limits the distribution of these soils within their respective districts. Within the Wollongbar, Dorrigo, and Ben Lomond districts the krasnozems are confined to basalt, podzolic soils being developed on other parent materials. Similarly in the Glen Innes and Inverell districts where, under milder weathering conditions, basalt gives rise to black earths and acid rocks to podzolic soils, the krasnozems are confined to fossil laterite formations. Laterite parent material explains the much lower phosphate content of the Inverell soil compared with the basalt krasnozems. Also fundamental differences between the laterite formations explain the much lower total, 'free', and gibbsite aluminium contents, the higher total and 'available' manganese, and the higher total phosphate in the Glen Innes compared with the Inverell

krasnozem. The Glen Innes laterite, according to Hallsworth and Costin (1953), was formed during the Pleistocene under conditions favouring the accumulation of iron and manganese, but not aluminium. The Inverell laterite, however, corresponds to the widespread Miocene or Pliocene formation (Hanlon, 1944; Hallsworth and Costin, 1953) and to the rich aluminium deposits termed 'bauxite' by Owen (1949).

The widely contrasting differences in the nature and density of the virgin vegetation in the districts studied are clearly a function mainly of climate. For this reason the trends in organic matter between the districts are a function of climate rather than vegetation. Effects of vegetation are, however, shown by the differences between the virgin and cultivated soils in the Wollongbar, Dorrigo, and Ben Lomond districts. Similarly the higher contents of organic carbon, nitrogen, and exchangeable metal cations in the upper horizons of the profiles, and the consequent decreases with depth are attributable to surface additions of vegetable debris.

Apart from their purely pedological significance, the results point to important trends in the fertility of the soils. In particular, comparison of the virgin and cultivated profiles indicates losses of nitrogen, organic phosphorus, exchangeable cations, and 'available' manganese in the Wollongbar, Dorrigo, and Ben Lomond districts. In a later paper losses of inorganic phosphorus as well will be described. In the case of the Wollongbar and Dorrigo cultivated soils which had been under paspalum pasture for 23 and 12 years respectively prior to sampling, the organic carbon has reached levels close to that in virgin soils. From the present results, however, there is no indication of a corresponding replenishment (or maintenance) of nitrogen or organic phosphorus levels. Furthermore, it appears that in the case of nitrogen the position is being aggravated by the addition of carbonaceous organic matter which, by widening the C:N ratio, may be favouring microbial immobilization of nitrogen.

The distribution of nutrient cations in the virgin profiles, from relatively high levels at the surface to very low levels with depth, suggests a closed cycle in which the cation requirements of virgin vegetation were supplied by leaf litter. The replacement of this vegetation with crops and pastures appears to have interrupted such a cycle and replaced it with an exploitative system. The consequent loss of cations points to the likelihood of deficiencies, particularly in the Dorrigo and Wollongbar soils where the levels of cations are very low. A potassium deficiency seems most likely, particularly in view of the potassium deficiencies that have recently been reported for similar soils in Victoria (Drake and Kehoe, 1956; Paton, 1956).

The contribution of the organic matter to the exchange capacity of these soils is noteworthy. By far the greater part of the cation-exchange complex in the surface horizons is organic. Indeed, in the Inverell soil, 5v, practically the whole of the cation-exchange capacity appears to be associated with the organic matter. The obvious implication of this observation is that loss of organic matter, which can accompany exploitative agriculture, threatens not only the nutrient content but also the capacity of the soils to retain cations.

Acknowledgements

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SOME CHEMICAL CHARACTERISTICS OF 'TERMITE SOILS' IN KENYA COFFEE FIELDS

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WITH PLATE

Summary

Chemical data are presented for a number of related topsoil, subsoil, and termite-soil samples collected in mulched coffee established on a laterized red loam coffee soil.

The comparisons of mean values for soil organic carbon, total base-exchange capacity, total exchangeable bases, exchangeable calcium, and exchangeable magnesium show that there is no statistically significant mean difference between the topsoil and termite-soil sample results. The subsoil sample results, however, are significantly lower than either the topsoil or termite-soil samples in all these results.

Similar comparisons of the mean values for soil pH and exchangeable calcium plus magnesium, when expressed as a percentage of the total exchangeable bases, show that the soil has been altered by *Odontotermes badius* (Hav.) in constructing the 'runs'; it is left with a higher pH value and with an increased proportion of the total exchangeable bases present as calcium plus magnesium.

It is not possible from these results to say conclusively whether the termite-soil samples are derived from the adjacent topsoil or subsoil.

It is concluded that the presence of the termite soil which eventually becomes intimately mixed with the topsoil during cultivation and weed-control operations is not a point to be considered against *Odontotermes badius* (Hav.) when assessing the 'pros and cons' of its presence in mulched coffee.

Introduction

THE activities of the termite *Odontotermes badius* (Hav.) in the soils of the drier coffee-producing areas of Kenya frequently give rise to speculation and conjecture regarding the overall benefit or harm which may derive from their presence. With the increase during recent years in the practice of mulching coffee in these areas, following the experimental results of Pereira and Jones (1950, 1954), observations indicate that the activities of these arthropods hasten the decomposition and destruction of mulch-grass materials and thereby decrease the length of effective mulch life.

This study of termite soils[1] under mulched coffee was undertaken with the object of obtaining information which would assist in providing an overall assessment of the desirability or otherwise of controlling termite activity in mulched coffee. The specific questions asked were: (1) What are the chemical characteristics of a termite soil in relation to the adjacent topsoil and subsoil? and (2) Does the termite soil come from the topsoil or subsoil? Shallow cultivation between the rows of coffee trees carried out at the end of successive mulch cycles effects an intimate

[1] In this study, 'termite soil' refers specifically to covered 'runs' of soil constructed by the termite on the outside of Napier grass mulches laid in mature coffee (*Coffea arabica*).

mixture of termite soil and rich topsoil that would be undesirable if the termite soil were excessively acid and base-unsaturated, i.e. chemically unaltered subsoil brought to the surface from excavations of underground chambers and tunnels.

Termite Activity in Coffee Fields

The known activities of *Odontotermes badius* (Hav.) in a coffee field may be summarized as follows:

1. It has been stated by Pereira (private communication) that the soil-burrowing activities of the termite, particularly in the topsoil, are extremely beneficial, since the effect is to increase the rate of rainfall infiltration through the soil surface and to bring about a greater degree of soil aeration, both to the topsoil and to the subsoil in the region of the deeper coffee-root system.

2. In this latter respect it is not uncommon to observe in the subsoil, usually at depths of between 2 and 4 ft., a high degree of fine-root proliferation where a large coffee 'vertical' root, i.e. a member of the axial-root system, has grown into an infilled termite tunnel. Compared with the surrounding subsoil the infill, which contains a proportion of topsoil washed downwards, is usually darker in colour, richer in plant foods, less compact, and is thoroughly explored by the many fine feeding roots developed.

3. The construction of fungus garden chambers in the subsoil, usually between 2 and 5 ft. below the soil surface, and of tunnels is carried out in the manner described by Fuller (1915) and more recently by Coaton (1947). Seldom, however, is there even a suspicion of a surface mound, the result, presumably, of frequent hand weeding and cultivations in the coffee.

4. Termites will often strip the dead bark off the entire coffee tree, but this apparently has no harmful results.

5. They destroy organic mulch material laid in the coffee. When they are working in mulch materials on the soil surface they construct covered 'runs' of soil on the outside so that they can carry out their activities in the dark. With particular reference to Napier grass (*Pennisetum purpureum*) which is grown for the purpose of mulching coffee, termites are very active inside the stalks (canes) as well as on the outside, leaving a residue of hollowed-out stalk filled with soil galleries inside (see Plate).

Soil Samples

During the latter half of 1954 a number of samples of termite soil were collected from several coffee fields on the Coffee Research Station, Ruiru. Samples were obtained by scraping the 'runs' from the outside of Napier-grass stalks in residual mulches which had been laid in the coffee before March 1954, i.e. before the long-rains period of April to early June. For each sample of termite soil collected, a single topsoil (0–6 in.) and subsoil (18–24 in.) sample was taken in the immediate vicinity. All the samples were collected in coffee growing on the Kikuyu red loam soil type (Gethin Jones, 1948). It seemed unlikely

that the termites would transport the soil from any great distance away on the soil surface, but it was recognized that soil might be brought up from a greater depth than 18–24 in. However, the general chemical pattern of the Kikuyu red loam soil profile, i.e. the change of chemical characteristics with increasing depth, is known to a depth of 10 ft., and it was assumed in the beginning that a comparison of chemical data between related termite-soil topsoil and subsoil samples might indicate the most probable source and would provide information on the first question posed.

The samples were prepared for analysis by air-drying in the laboratory and grinding to pass a 2-mm. round-hole sieve. Coarse organic debris (macro-organic matter) was picked out from the samples, especially from the termite-soil samples, by hand forceps. Comparisons between the three soil samples in each related group were made in terms of soil colour, pH value, organic-carbon content, total base-exchange capacity, total exchangeable bases, exchangeable calcium, and exchangeable magnesium contents. All the determinations except colour comparisons were carried out in duplicate on individual samples.

Results and Discussion

1. *Soil colour*

In an attempt to describe more precisely the individual colours of related termite-soil, topsoil, and subsoil samples the Munsell Soil Colour Chart was used, but this technique proved to be unsatisfactory because of the small, though observable, colour differences. However, when the air-dried samples were mounted on a white card in groups of three, a consistent difference was apparent. The termite-soil samples were generally paler in colour than either the related topsoils or subsoils. The general colour designations of the topsoil and subsoil samples were Hue 5 YR 4/4 reddish brown, for topsoils, and Hue 5 YR 4/6–4/8 yellowish red for subsoils. The termite-soil samples were more strongly inclined to the yellowish red coloration, Hue 5 YR 4/8.

2. *pH values*

The pH values were determined with a glass-electrode pH meter on a soil-paste mixture (Methods of Analysis, A.O.A.C., 1950), and subsequently some of the samples were examined using the M/100 calcium-chloride method of Schofield and Wormald Taylor (1955), but with a 1:5 and not a 1:2 soil:M/100 $CaCl_2$ ratio.

TABLE 1

pH Values

Method	*Termite soil*	*Topsoil*	*Subsoil*
Soil paste (A) (means of 12) .	5·89	5·62	5·52
M/100 $CaCl_2$ (B) (means of 6) .	5·57	5·21	5·23

S.E. method (A) = ±0·07, L.S.D. 5% = 0·15; 0·1% = 0·27.
S.E. method (B) = ±0·10, L.S.D. 5% = 0·23; 1% = 0·33.

The mean values for the topsoil and subsoil samples show very little difference when the determination is carried out by either method, whereas the termite-soil sample means are very significantly greater than the topsoil means by both methods, i.e. the samples have a lower degree of acidity. In fact, only two of the termite-soil samples had values which were slightly lower than the related topsoil samples and all of them were greater than the related subsoil-sample values.

3. *Organic carbon*

A sub-sample was drawn from each of the samples and was ground to pass through a 0·5-mm. round-hole sieve before determining the Walkley–Black value. The figures recorded in Table 2 are expressed on an oven-dry (100° C.) soil basis.

TABLE 2

Walkley–Black Organic-Carbon Values (uncorrected)
(mg. carbon/g. oven-dry soil)

Sample reference	*Termite soil*	*Topsoil*	*Subsoil*
A1	22·82	30·14	11·83
A2	22·71	21·23	11·50
C2	29·11	27·97	12·28
E2	13·20	15·11	8·73
F1	24·78	25·99	11·64
F2	16·05	23·66	12·14
Mean	21·59	24·02	11·35

S.E. of the mean = ±1·76; L.S.D. 5% = 3·92; 1% = 5·58.

There is no significant difference in the mean Walkley–Black organic-carbon values between termite-soil and topsoil samples, but the mean value for the subsoil samples is very significantly lower. Only the data for the F2 samples provide a termite-soil figure which is closer to the subsoil than the topsoil figure. A similar relationship is noted for the total base-exchange figures for the F2 samples (Table 3).

4. *Total base-exchange capacity*

These determinations were made by the rapid copper-acetate technique after Cornfield (1952), using a centrifuge to hasten the liquid/solid separations during the replacement phase.

In the average Kikuyu red loam profile the total base-exchange capacity decreases with depth, e.g. 0–6 in. = 16·25, 18–24 in. = 11·55, and 84–96 in. = 10·25 m.e./100 g. air-dry soil. The soils in Table 3 would have air-dry moisture contents of between 3 and 5 per cent. on an oven-dry-weight basis.

A comparison of the mean values for these samples shows that only the difference between the subsoil and either the topsoil or the termite-soil samples is significant. The difference between termite-soil and

topsoil samples is not significant. An inspection of the individual values in the table shows that in three comparisons, i.e. B1, D1, and F2, the termite-soil figures are apparently more closely related to those of the subsoil than the topsoil. A strict interpretation of these data would seem to support the contention that in the greater number of cases the termite soil originated from the immediate topsoil zone, and not from the subsoil. The possibility of increased base-exchange activity as a result of

TABLE 3

Total Base-Exchange Capacity (m.e./100 g. air-dry soil)

Sample reference	*Termite soil*	*Topsoil*	*Subsoil*
A1	20·2	20·3	14·0
B1	17·5	21·6	16·7
C1	18·2	19·2	12·7
D1	13·3	16·2	12·5
E1	18·7	18·7	12·5
F1	19·7	19·7	13·3
A2	16·2	19·2	11·7
B2	15·5	19·2	12·7
C2	21·2	18·8	11·5
D2	18·2	20·8	13·5
E2	15·2	13·3	13·3•
F2	15·3	19·2	14·2
Mean	17·4	18·9	13·2

S.E. of the mean = ±0·8; L.S.D. 5% = 1·7; 0·1% = 3·2.

• Sample from an eroded coffee area.

the addition by the termites of colloidally active organic matter is not adequately supported by the data in Table 2.

5. *Total exchangeable bases, exchangeable calcium, and exchangeable magnesium*

The rapid extraction of these fractions was carried out with neutral, normal ammonium acetate using a centrifuge technique. The total exchangeable bases were determined by the method described in the Methods of Analysis, A.O.A.C. (1950). Calcium, and magnesium by difference, were determined by the volumetric versenate-titration method (U.S.D.A. Handbook, 1954). It seems probable, in the light of a paper by Hoffman and Shapiro (1954) which subsequently came to hand, that the values obtained for magnesium are on the high side, but they are considered here to be none the less comparable because of this.

There are no statistically significant differences between the termite-soil and topsoil-sample means, but the subsoil-sample means are significantly lower than either of the former for all three sets of data. This again emphasizes the similarity between the chemical characteristics of the termite-soil and the topsoil samples. It will be noted that whilst the termite-soil samples have a mean T.E.B. value which is slightly less

than that of the topsoil samples, the mean values for exchangeable calcium and magnesium are greater. In Table 5 the mean values are given for exchangeable calcium, exchangeable magnesium, and exchangeable calcium plus magnesium expressed as a percentage of the total exchangeable bases of each soil sample.

TABLE 4

Total Exchangeable Bases, Exchangeable Calcium, and Magnesium (m.e./100 g. air-dry soil. Means of 6)

	Termite soil	*Topsoil*	*Subsoil*	*S.E.*	*L.S.D.*
T.E.B. . .	14·53	16·77	11·95	±1·20	5% = 2·67 1% = 3·80
Exch. Ca .	9·23	8·87	6·13	±0·61	5% = 1·36 1% = 1·93
Exch. Mg .	4·88	4·34	3·19	±0·27	5% = 0·60 1% = 0·86

TABLE 5

Exchangeable Calcium, Exchangeable Magnesium, and Exchangeable Calcium plus Magnesium expressed as a percentage of the Total Exchangeable Bases (Means of 6)

	Termite soil	*Topsoil*	*Subsoil*	*S.E.*	*L.S.D.*
Exch. Ca .	63·9	50·6	50·9	..	No sig. diff.
Exch. Mg .	29·5	25·3	26·5	..	No sig. diff.
Exch. Ca+Mg.	93·5	75·9	77·3	±6·1	5% = 13·6

N.B. Statistical calculations were carried out after making angular transformations of the percentage data.

Expressed in this manner it appears that a much higher percentage of the exchangeable bases in the termite-soil samples consist of calcium plus magnesium than in either the topsoil or subsoil samples, and that the latter have closely similar percentage contents of these cations. This is in agreement with the pH values recorded in Table 1, particularly those obtained for the same eighteen soil samples by the M/100 calcium-chloride method. This evidence suggests that the termites may have altered in some way the relative proportions of some of the basic constituents of the soil-exchange fraction in their use of the soil. This type of alteration is considered to be advantageous on these acid red soils.

Hesse (1955), in his study of the chemical and physical nature of termite-mound soils in East Africa, found that they 'are built from the subsoil and that termites do not directly alter or affect the chemical characteristics of the soil with the possible exception of base-exchange capacity and total exchangeable bases'.

Mechanical analyses of related termite-soil, topsoil, and subsoil

samples in this work failed to differentiate clearly between samples as to the original source of the termite soil, perhaps because the clay fraction (International system) in the Kikuyu red loam soil is so high, i.e. usually more than 65 per cent. In the samples examined, the greatest variation occurred between sand fractions (coarse and fine sand) with mean values of 10·5 per cent. for the topsoils, 6·8 per cent. for the subsoils, and 6·1 per cent. for the termite soils. The almost constant mean values obtained for the silt and clay fractions are reflected in the ratios of coarse plus fine sand to silt plus clay which were 1 : 7·9 for topsoils, 1 : 11·9 for subsoils, and 1 : 13·7 for termite soils respectively; these results, whilst pointing to a subsoil origin of the termite soils, are not considered to be conclusive.

The mean results for pH determination (Table 1) and the percentage calcium plus magnesium in the total exchangeable bases (Table 5) suggest that the termites do alter the quantities of exchangeable calcium and magnesium in the soil they work with. Irrespective of whether the termite-soil material is derived originally from a topsoil or subsoil source, it has finally a higher percentage content of calcium plus magnesium in the total exchangeable bases, and a higher pH value than either the topsoil or the subsoil.

The mean results of the pH and chemical determinations show quite clearly that, on the average, the termite soil *in situ* is more closely related to the topsoil than to the subsoil samples collected for this study.

With regard to the original source of the soil used by the termite, these results do not provide for a clear interpretation, since both the mean results of all the different chemical determinations made and the individual results for related samples given in Tables 2 and 3 might be interpreted in one of two ways. Either this arthropod has substantially altered the subsoil in most cases, until the results obtained by chemical analysis more nearly resemble those of the related topsoil samples, or it would appear to be relatively non-selective with regard to its building material for covered 'runs' in this soil type, and these results simply reflect a behaviour pattern determined by individual circumstances at the site of the building operations, e.g. whether, by chance, topsoil or subsoil material was used as a matter of convenience. The former alternative would be in agreement with the work of Hesse (1955) on termite-mound soils in East Africa, and is favoured by Harris (personal communication), who states: 'It would be reasonable to assume from the deep nest system of *badius* and its lack of interest in the humus of topsoil as food, that covered ways are constructed from subsoil, and that, as in the case of the large-mound builders, grains of sand carried in the mandibles are held together with a mortar of clay and saliva regurgitated from the termite's crop.' Could it be that the additional calcium plus magnesium found in the termite soils is derived from the termite's saliva?

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Napier-grass stalks (canes) from a residual coffee mulch showing (*a*) termite soil (*Odontotermes badius* (Hav.)) adhering to the outsides, and (*b*) termite soil constructions inside the stalk where termites have been working

J. B. D. ROBINSON—PLATE I

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STUDIES ON THE BASALTIC SOILS OF NORTHERN IRELAND

III. EXCHANGEABLE-CATION CONTENTS OF SAND, SILT, AND CLAY SEPARATES

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Summary

Results are given of the exchangeable calcium, magnesium, sodium, and potassium contents of the sand, silt, and clay fractions separated by purely physical methods from sixteen horizons, mainly subsoils from basaltic soil profiles in Northern Ireland. Relatively high exchangeable-calcium values are recorded, ranging from 6·9 to 20·9 m.e. per cent. for sands, from 9 to 28 m.e. per cent. for 'silts', and from 8·3 to 35 m.e. per cent. for clay separates.

Exchangeable-magnesium values are also high, particularly for separates from subsoils with imperfect drainage, and values as high as 17·2, 27·3, and 32·2 m.e. per cent. are recorded for sand, silt, and clay separates, respectively. The exchangeable-magnesium contents usually increase with depth in the subsoil and in many cases the exchangeable-magnesium values for silts are as high as or higher than values for corresponding clay separates. Comparisons of the values for sands, 'silts', and for corresponding clays suggest that the high values exhibited by the silts (and often by the sands) cannot be attributed, to any considerable extent, to incomplete dispersion, e.g. to the presence of normally dispersible clay aggregates in the silts or sand separates. It is suggested that these high values and the associated high cation-exchange capacities of these silts (and coarser fractions) may be due to the presence of partially weathered rock minerals which may be broken down, e.g. by acid treatments and dispersion procedures prior to detailed examinations.

In neutral and slightly acid soils calcium is generally found to be the main exchangeable metal cation, but there are many references in the literature to such soils in which the exchangeable-magnesium contents approach or even surpass the quantities of exchangeable calcium. Mitchell (1937), Hallsworth *et al.* (1952), Glentworth (1954), and Brown (1954) have recorded values of the order of 20–25 m.e. exchangeable magnesium per 100 g. soil for some subsoil horizons of basic igneous soils, and Kelly (1948) has recorded a value of 40 m.e. per cent. for a heavy clay from California. Such high values are usually associated with imperfect drainage conditions and often, but not always, with high clay contents. In a recent paper on basaltic soils in Northern Ireland McConaghy and McAleese (1957) gave results showing appreciable increases in exchangeable magnesium with increasing profile depth, although the percentage clay contents showed considerable decreases

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with depth. Examination of clay separates from such profiles usually showed relatively little change in the exchange capacity values with depth but the exchange capacity of silt fractions was found to increase very significantly with depth and in subsoil horizons to reach values of 50 m.e. to 60 m.e. per cent.—i.e. as high as or higher than those for corresponding clay separates (McAleese and McConaghy, 1957). Sand fractions were also found to have appreciable exchange capacities. The present paper records the results obtained in investigations into the quantities of individual exchangeable cations present in clay, silt, and sand separates from these basaltic soils.

Experimental

Samples, mainly subsoils from one or more horizons of ten basaltic soil profiles, were used in this work. A description of the soils is given in an earlier paper (McConaghy and McAleese, 1957).

Sand, silt, and clay separates were isolated by purely physical means. It was realized that separation in this way would not be as effective as separations employing chemical and physical dispersion agents and that separates of 'silt' size or coarser fractions might still contain some finer particles.

To eliminate the cementing action of organic matter and the need for peroxide pre-treatment all the samples (with two exceptions) were from subsoil horizons containing little organic carbon. Both freshly dug and laboratory-dried samples were used in this investigation. Known weights of the freshly dug samples were transferred to glass-distilled water to prevent drying out which might result in fixation of part of the exchangeable magnesium or increased cementation of the clay particles through oxidation, e.g. of ferrous compounds which might be present. The soil was soaked for 24 hours in glass-distilled water, mixed by a strong glass rod and the suspension stirred for 12 hours with a high-geared (stainless-steel) stirrer to which glass baffles were attached. The suspension was shaken by hand for 5 minutes and allowed to settle. Silt-sized fractions were separated from the silt and clay suspensions by repeated sedimentation and decantation of the clay suspensions until clear supernatants were obtained. The combined clay suspensions and combined 'silt' suspensions were redispersed by shaking in distilled water and centrifuged according to the method of Jackson (1949).

The combined suspensions were evaporated to small volume on a water-bath, then centrifuged and the supernatant liquid siphoned off carefully. This liquid was concentrated to about 50 ml. and reserved for spectrographic analysis to determine the cation concentration. The clay and silt separates were shaken twice with neutral 95 per cent. methyl alcohol and freeze-dried, employing 'Speedivac' pump in conjunction with phosphorus pentoxide in vacuum desiccators (Parish, 1953). After drying the soil separates were weighed in order to compare the results of physical separation with those obtained by chemical-dispersion procedures, to have some measure of the efficiency of the physical-dispersion method. Samples of the freshly dug soils were dried at 105° C. for 24 hours to determine moisture contents. The clay

separates dried out in hard lumps which were ground in an agate mortar to pass a 100-mesh sieve. The silt separates crumbled under the slightest pressure. They were also ground to pass the 100-mesh sieve. The separates were brought to 50 per cent. relative humidity by placing over glycerol solutions for periods up to 7 days.

The sand separates (coarse and fine) were shaken with 95 per cent. methyl alcohol to remove excess water, dried in the oven at 60° C. for 6 hours, cooled, and weighed. They were then placed over glycerol solutions to bring to 50 per cent. relative humidity.

For the determination of exchangeable cations, samples (2 g. clay, 2 g. silt, or 20 g. sand) were leached with 500 ml. neutral normal ammonium acetate. The leachates were evaporated to dryness, oxidized twice with aqua regia, and the residues taken up in 5 ml. N/2 HCl, heated, diluted, filtered, and made up to 50 ml. Individual cations were determined by the spectrographic technique described by Mitchell (1948).

Results

Spectrographic analysis of concentrates of the clear supernatant liquids (siphoned off in the course of the separations described above) showed that there was no magnesium in any of the supernatants, and only traces (less than 0·03 mg. per litre) of calcium.

The exchangeable-cation contents of the individual separates are given in Table 1. No distinction has been made here between results for separates from air-dry and from freshly dug soils which are denoted by an asterisk.

The exchangeable-calcium contents of the coarse and fine sands range from 6·9 to 20·9 m.e. per cent., while those of the silts range from 9 to 28 m.e. per cent., and those of the clay separates from 8·3 to 35 m.e. per cent. For the sands the values often show some increase with depth in the profile, but for the silts and clay fractions it is quite common to find lower Ca values in the C or CG horizons than in the B or BG horizons. The exchangeable-calcium values for the sand and silt fractions are sometimes remarkably high. A few values for sand separates approach or surpass the corresponding values for the silt fractions and occasionally approach the values for corresponding clay separates.

Exchangeable-magnesium values range from 0·8 to 17·2 m.e. per cent. in the sands, from 3·9 to 27·3 m.e. per cent. in the silt-sized fractions, and from 2·0 to 32·2 m.e. per cent in the clay fractions. There is usually an appreciable increase in values with increasing depth in the profile, but this may not apply for profiles with free drainage. The lowest exchangeable-magnesium values recorded in Table 1, i.e. 0.8 m.e. per cent. and 2·0 m.e. per cent., are for the sand and clay fractions respectively from the B_3 horizon of a freely drained profile. The only other low value (3·9 m.e. per cent.) is for the silt fraction from a surface horizon, the lowest value for a subsoil silt being 8·2 m.e. per cent.

In seven out of sixteen results the exchangeable-magnesium contents of the silts are higher than the values for corresponding clays, and only for the surface horizon (profile 9) is the value for silt appreciably lower than the value for the corresponding clay. One unusual feature of the

TABLE I

Exchangeable Metal Ions in Sand, Silt, and Clay Separates from Basaltic Subsoils

Profile	*Drainage*	*Horizon*	*Depth (in.)*	*Exchangeable metal ions (m.e. %) in:*											
				Sand				*Silt*				*Clay*			
				Ca	*Mg*	*K*	*Na*	*Ca*	*Mg*	*K*	*Na*	*Ca*	*Mg*	*K*	*Na*
1. Water Commissioners*	Free	C	30+	15·6	7·3	0·22	1·0	15·8	13·1	0·36	0·83	27·1	10·7	0·35	1·38
2. Frocess	Free	B_2	15–24	6·9	0·8	0·32	0·7	9·0	8·4	0·52	0·64	8·3	2·0	0·31	0·56
		C	24+	8·1	9·3	0·70	1·0	19·2	18·8	0·77	1·20	22·0	13·5	0·14	2·28
3. Rashee I	Good	S	8–15	17·6	5·8	0·19	0·47	28·0	16·8	0·15	0·23	27·5	16·5	0·34	0·94
		B_2	15–30	16·0	10·9	0·14	0·90	24·7	21·0	0·15	0·52	18·4	24·9	0·31	1·03
4. Rashee II*	Good	C	30+	14·3	7·9	0·21	0·98	11·5	13·3	0·41	0·75	19·8	10·0	0·31	0·95
5. Monaghan*	Good	B_2	12–20	20·9	7·8	0·14	0·69	19·1	17·2	0·34	1·03	22·0	18·4	0·32	1·27
		C	20+	13·0	12·3	0·71	1·07	20·5	18·6	0·66	0·94	22·8	20·0	0·85	1·23
6. Beltoy	F. Good	G_2	16+	11·5	8·3	0·28	1·16	17·1	19·0	0·29	0·53	22·2	19·8	0·26	0·97
7. Carnanee	Fair	G_2	20+	14·3	10·5	0·14	0·49	12·7	27·3	0·15	0·37	20·8	29·1	0·81	1·00
8. Glynn Hill	Poor	G_2	15–20	12·3	4·1	0·28	0·79	27·3	8·2	0·15	0·44	35·0	10·8	0·78	0·84
		G_2	20+	15·1	7·1	0·33	1·34	18·8	25·1	0·29	0·56	29·7	16·1	0·91	0·92
9. Ballyno	Poor	S	0–8	13·8	4·9	0·23	0·48	24·0	3·9	>0·15	0·48	23·5	7·5	0·45	0·92
		G	20*	18·1	7·6	0·15	0·61	24·2	17·8	0·15	0·36	14·8	30·1	0·34	1·14
10. Straidhavern*	Impeded	G_1	8–16	7·0	4·2	0·13	0·60	17·9	27·3	0·44	0·92	23·0	21·6	0·42	1·02
		G_{2-3}	16+	14·5	17·2	0·14	0·80	20·9	25·3	0·38	0·78	19·1	32·2	0·46	1·03

* Fresh samples—not dried in laboratory before dispersion.

results recorded in Table 1 is that the exchangeable-magnesium contents of fractions from a well-drained profile (Rashee I) are shown to be higher than corresponding results from a poorly drained profile at Glynn Hill, but it is probable that these results may be due to differences in the magnesium contents of the respective parent materials.

Exchangeable-potassium values range from 0·13 to 0·71 m.e. per cent. for sands, from 0·15 to 0·77 m.e. per cent. for silts, and from 0·14 to 0·91 m.e. per cent. for clays. The general trend of values is that indicated by the averages, which are 0·27 m.e. per cent for sands, 0·34 m.e. per cent. for silts, and 0·47 m.e. per cent. for clays. The exchangeable-potassium values of the silts isolated from samples fresh from the field (indicated in Table 1 by an asterisk) are always appreciably higher than the values for those silts isolated from laboratory-dried samples. The averages are 0·49 and 0·19 m.e. per cent. respectively. The extent and the consistency of the differences would suggest that laboratory drying has resulted in the fixation of part of the potassium in the silts, though no similar fixation is suggested from the results for the clay separates.

Exchangeable-sodium contents range from 0·47 to 1·34 m.e. per cent. with an average of 0·75 m.e. per cent. in the sands, from 0·23 to 1·2 m.e. per cent. with an average of 0·65 m.e. per cent in the silts, and from 0·56 to 2·28 m.e. per cent. with an average of 1·09 m.e. per cent in the clays. The general trend is again the same as that of the averages, the lowest average being that for the silt fractions. For each of the separates the exchangeable-sodium contents tend to rise with depth, which is in agreement with the exchangeable-sodium values recorded for the soils (McConaghy and McAleese, 1957). The exchangeable-sodium values of the silts isolated from fresh samples are also found to be appreciably higher than those for silts separated from laboratory-dried samples.

Discussion

Under imperfect drainage conditions there is a reduction in losses of weathering products from the soil profile. This may result in the exchangeable-cation contents being maintained at a relatively uniform level throughout the profile, or in an actual accumulation of cations in the subsoils. But this 'reduction in losses' of cations, or the actual accumulation of cations, does not affect all cations to the same extent and, while exchangeable-magnesium contents may increase markedly with depth under poor drainage conditions, there is not necessarily any such increase with depth in the amounts of other exchangeable cations, e.g. calcium. Under such conditions there is generally a decrease with depth in the ratios of exchangeable calcium to exchangeable magnesium, and results quoted by Glentworth (1954) for basic igneous soils in Aberdeenshire agree closely with values obtained by the authors for similar types of profiles in Northern Ireland.

Table 2 records the exchangeable-calcium/exchangeable-magnesium ratios for sand, silt, and clay separates from the sixteen soil horizons examined. The relatively low ratios for the sands reflect the high magnesium contents of the coarser fractions and of the parent materials. The ratios are of the order of 1·0 or less for all the *subsoil* silts except

that for the G_2 horizon at Glynn Hill (profile 8). The ratios are seldom lower for clay fractions than for the corresponding silt-sized fractions, and indeed in nine of the sixteen horizons they are higher for the clays than for the corresponding silts.

TABLE 2

Exchangeable-Ca/Exchangeable-Mg. Ratios for Sand, Silt, and Clay Fractions from Basaltic Soils

Profile	*Horizon (in.)*	*Exchangeable Ca/Mg for:*		
		Coarse and fine sand	*Silt*	*Clay*
1	C 30+	2·1	1·2	2·5
2	B_3 15–24	7·7	1·1	4·2
	C 24+	0·9	1·0	1·6
3	S 8–15	3·0	1·7	1·7
	B_2 15–30	1·5	1·2	0·7
4	C 30+	1·8	0·9	2·0
5	B_2 12–20	2·7	1·1	1·2
	C 20+	1·1	1·1	1·1
6	G_2 16+	1·4	0·9	1·1
7	G_2 20+	1·4	0·5	0·7
	G_3 15–20	3·0	3·3	3·2
	G_3 20+	2·1	0·8	1·8
9	S 0–8	2·8	6·2	3·1
	G_2 20+	2·4	1·4	0·5
10	G_1 8–16	1·7	0·7	1·1
	G_{2-3} 16+	0·8	0·8	0·6

Magnesium obviously makes up an appreciable proportion of the exchangeable metal cations which are present in these separates (Table 3), the contribution of magnesium to the total metal-cation content being particularly high under imperfect and under impeded drainage conditions. The degree of magnesium saturation appears to increase with depth—sometimes considerably as in the Glynn Hill profile.

All separates exhibit this general increase with depth, and it is interesting to see that the degree of magnesium saturation of the silt separates in many cases is higher than that of corresponding clay separates.

Mechanical-analysis results already recorded (McConaghy and McAleese, 1957) have shown that the clay contents of basaltic soil horizons usually fall noticeably with depth, though no corresponding decreases are found in the cation-exchange capacities. As the clay contents decrease, the coarser fractions must increase in quantities and such increases are usually reflected in increased silt contents.

The cation-exchange capacities of the silts have also been shown to increase with depth (McAleese and McConaghy, 1957), and it is now

TABLE 3

Exchangeable Magnesium as Percentage of Total Exchangeable Metal Cations

Profile	*Horizon*	*Exch. Mg as percentage of total exchangeable metal ions in:*		
		Sand	*Silt*	*Clay*
Water Commissioners .	C	30·1	43·6	27
Frocess	B_3	9·5	45·2	17·5
	C	48·6	47·0	35·6
Rashee I . . .	S_2	23·9	37·1	36·4
	B_2	38·8	45·3	55·5
Rashee II . . .	C	33·6	51·2	32·1
Monaghan . . .	B_2	26·4	45·6	43·8
	C	45·3	45·7	44·4
Beltoy	G_2	38·5	51·1	45·7
Carnanee . . .	G_2	41·1	67·1	56·0
Glynn Hill . . .	G_2	23·1	22·6	22·5
	G_3	29·5	56·1	33·6
Ballyno	S	25·1	13·6	22·7
	G_1	28·6	41·8	64·7
Straidhavern . . .	G_1	35·3	58·5	47·9
	G_{2-3}	52·7	53·4	60·8

evident that the exchangeable-magnesium contents together with the degree of magnesium saturation of the silts also increase with depth. It is not surprising, therefore, to find that there is an apparent correlation between the exchangeable magnesium and the silt contents of these basaltic soils. This is illustrated in Fig. 1, though it should be noted that the data used in preparing Fig. 1 relate to unclassified samples irrespective of their position in the soil profile or of the existing pedological conditions. No such relationship can be shown for exchangeable-magnesium and clay contents for these samples (Fig. 2), as the former values usually increase while the clay contents decrease with depth.

The actual contributions by individual separates to the total exchangeable-magnesium contents of the subsoils are shown in Table 4, which also includes exchangeable-magnesium values determined directly on the subsoils. Summation values (col. 9) agree well with the values determined on the composite samples, and this supports the view that magnesium leached by neutral normal ammonium acetate is truly exchangeable. It also indicates that the magnesium which is released is unaffected by the method employed for the isolation of these separates.

The degree of dispersion attained by purely physical methods in the course of these studies was usually between 85 and 93 per cent.—based on the yields of clay relative to the quantities of clay determined by the

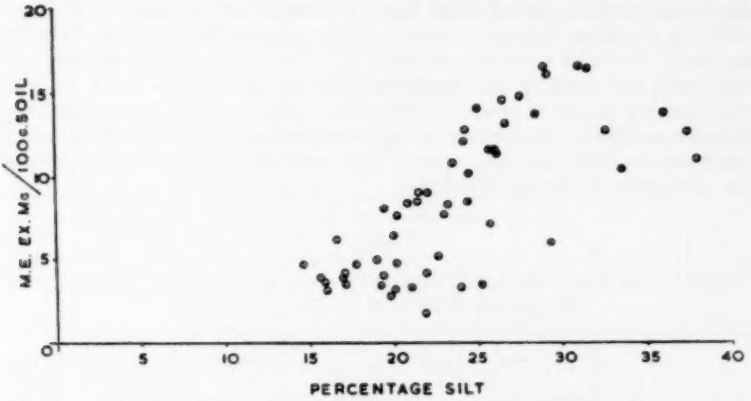

FIG. 1. Relationship between percentage silt and the exchangeable magnesium of basaltic soils of N.E. Ireland

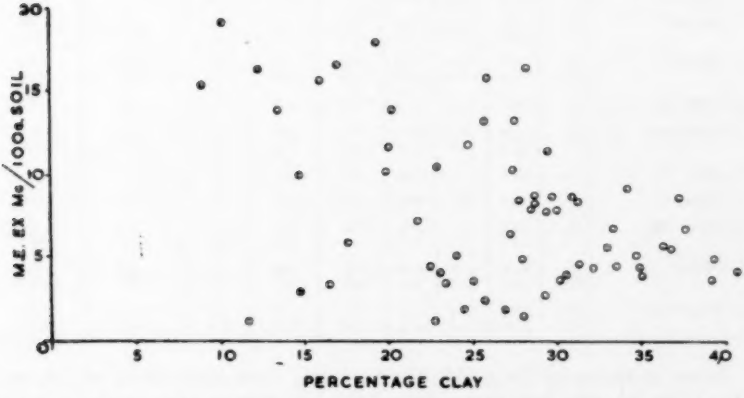

FIG. 2. Relationship between percentage clay and the exchangeable magnesium of basaltic soils of N.E. Ireland

International soda method of mechanical analysis. The 'silt' yields (usually about 10 per cent. of the estimates) suggested that the remainder of the normally dispersible clay remained as silt-sized aggregates. There is reason to believe that the usual dispersion methods themselves (as in the International method) may not be completely efficient for these subsoils without some modifications, but it is obvious from the comparisons of exchangeable-magnesium values for clays and 'silts' shown in Table 1 that the high values for the silt-sized fractions cannot be considered as due only to the presence of undispersed clay. Physical characteristics alone of the dried silts suggested that relatively little clay can be present, the difference between the dried silts and the

hard nature of the dried clays having been already mentioned. In the field the so-called 'heavy' basaltic soils dry out in hard clods and there is no doubt that this tendency to hard and cloddy structures is associated only with the amount and nature of the clay and particularly with the clay fraction which is readily dispersed. It is not associated, directly at any rate, with anything such as high magnesium contents, with the silt fractions, or with any amounts of clay minerals likely to be present in the silt-sized or coarser fractions.

TABLE 4

Contributions from Sand, Silt, and Clay Separates to Total Exchangeable-Magnesium Contents of Basaltic Soils

Profile	Horizon	Mechanical analysis			Exchangeable magnesium (m.e./100g. soil) contributed by:				Exchangeable magnesium by direct determination m.e. %
		% sand (c+f)	% silt	% clay	Sand (c+f) fractions	Silt fraction	Clay fraction	Summation of separate contributions	
1	2	3	4	5	6	7	8	9	10
1. Water Commissioners	C	44·3	31·4	10·9	3·2	4·1	1·2	8·5	7·5
2. Frocess	B_2	45·9	20·3	21·5	0·4	1·7	0·4	2·5	2·6
	C	50·2	26·8	11·0	4·7	5·0	1·5	11·2	11·4
3. Rashee I	S_2	29·4	27·9	28·5	1·7	4·7	4·7	11·1	11·7
	B_2	44·4	28·4	16·6	4·8	6·0	4·1	14·9	13·9
4. Rashee II	C	25·7	34·5	25·4	2·0	4·6	2·5	9·1	7·7
5. Monaghan	B_2	34·6	30·3	21·4	2·7	5·2	3·9	11·8	9·1
	C	43·5	34·0	11·7	5·4	6·3	2·3	14·0	12·4
6. Beltoy	G_2	28·6	26·6	32·2	2·4	5·1	6·4	13·9	13·3
7. Carnanee	G_2	46·1	25·5	26·4	4·8	7·0	7·7	19·5	17·9
8. Glynn Hill	G_2	26·6	27·0	40·7	1·1	2·2	4·4	7·7	5·6
	G_3	29·1	31·9	30·6	2·1	8·0	4·9	15·0	16·5
9. Ballyno	S	22·9	22·1	43·8	1·1	0·9	3·3	5·3	4·2
	G_1	32·5	36·2	23·9	2·5	6·5	7·2	16·2	13·9
10. Straidhavern	G_1	25·7	13·3	44·9	1·1	3·6	9·7	14·4	10·1
	G_{2-3}	31·1	31·0	24·3	5·4	7·9	7·8	21·1	19·8

X-ray analyses of clays (McAleese, 1954) from these soils which tend to exhibit 'cloddy' structures reveal the presence of the expanding type of clay minerals, and some clay minerals also appear to be present in the silt separates even after they are subjected to repeated and normally efficient dispersion procedures. The quantities of such clay minerals in the silts are not sufficient, however, to account entirely for their high exchange capacities or for their high exchangeable-magnesium contents. Perhaps partially weathered rock minerals may be formed in the early stages of weathering of basic igneous silicates, and the fact that there is no direct evidence available as yet of their presence in the resulting silts and clays may be due to their instability during pre-treatments.

On the other hand there is abundant evidence, e.g. Hosking (1948) and Joffe and Kunin (1944), that clay minerals may be present in considerable quantities in the coarser fractions of soils, particularly those derived from basic igneous materials. These 'coarser' fractions as

normally dispersed and separated from basaltic soils are certainly not entirely composed of primary unweathered materials.

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STUDIES ON THE BASALTIC SOILS OF NORTHERN IRELAND

IV. MINERALOGICAL STUDY OF THE CLAY SEPARATES ($< 2\mu$)

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Summary

The clay separates ($< 2\mu$) isolated from the horizons of ten basaltic soil profiles are shown by X-ray analysis to have a mixed mineralogical composition; the type and amount of each mineral present being dependent on the drainage conditions within the profile.

Kaolin, the end product of weathering, generally predominates in surface horizons. Vermiculite is formed in well-drained profiles, but where gleying symptoms are evident vermiculite is replaced by montmorillonite, the amount of which increases with increased degree of waterlogging. Illite occurs in only two profiles to any appreciable extent.

It is inferred that soil separates other than clay are contributing to the cation-exchange capacity of these soils.

In recent communications (McConaghy and McAleese, 1957; McAleese and McConaghy, 1957) very high exchange-capacity values were recorded for the basaltic soils of Northern Ireland. It was observed that whilst the exchange capacities remained either relatively uniform, or in a number of examples increased in value, with depth in the profile, there were corresponding decreases in clay and organic-matter contents down the profile. It was not possible to account for the total cation-exchange capacity (C.E.C.) of the soils in the lower horizons (where organic matter was absent or present in negligible amounts) from considerations based on the results of mechanical analyses and cation-exchange capacities of the clay separates.

The present investigation was undertaken to study the nature, profile distribution, and relative proportions of the clay minerals in relation to the high exchange capacities of the soils.

Experimental

Mechanical separations were made using ammonium hydroxide. Organic matter was removed with 6 per cent. hydrogen peroxide and the clay separates isolated by repeated sedimentation and decantation. The bulked suspensions were concentrated to small volume on a water-bath, oxidized again with 6 per cent. hydrogen peroxide, washed with 95 per cent. alcohol followed by benzene, and dried in the oven at 105° C. The 'free' iron oxides were removed from part of the clay by the sodium-hydrosulphite method of Mackenzie (1954). The clay separates were regarded as made up of material less than 2μ in diameter.

In the determination of the C.E.C. of the clays, the micro-distillation

procedure of Mackenzie (1952) was adopted. Schollenberger and Simon's method (1945) was used for the C.E.C. determinations of the soils.

Powder specimens, for X-ray analysis, were prepared by the method of MacEwan (1949) using 'Durofix', and preferentially orientated specimens by the pressure-aggregate technique of Mitchell (1953). Where heat treatment was given the samples were heated as aggregate flakes, or as a powder which was then made into powder specimens with 'Durofix'. A Hilger X-ray diffraction unit giving Co Kα radiation, and 9-cm. precision cameras were used.

Results and Discussion

The minerals and the estimated amounts found to be present in the clay separates, from horizons of ten profiles which are representative of a number of soil series classified on a hydrological basis, are given in Table 1. The figures in the table represent parts of ten and are based on the visual comparison of the intensity of the lines on photographs of the original samples, i.e. the clay separates as isolated by the International Method of mechanical analysis. Also recorded in Table 1 are the percentage clay contents, C.E.C. of the soils, and C.E.C. of the clay separates in m.e. per 100 g.

In Table 1 the basaltic soils are shown to have a mixed mineralogical composition comprising kaolin, illite, vermiculite, and montmorillonite in varying proportions. In the majority of the profiles studied, kaolin is the predominating mineral in clays from surface horizons, but there is generally a decrease in amount of this mineral with depth in the profile. Montmorillonite when present generally occurs in greatest amount in the lower horizons. Vermiculite occurs in eight out of the ten profiles studied, but with two exceptions the illite content is very small or absent from the basaltic soils.

Considering the profiles individually and in groups based on the soil series (as shown in Table 1) the following facts are observed. In the Carnanee profile where the drainage conditions are described as fair, there is a decrease in kaolin from 4·5 parts in the clay separate from the A horizon at a depth of 10 in. to 2·5 parts in the G_2 horizon at a depth of 20 in.+. The kaolinitic material gave a somewhat diffuse band around 7 Å. with maximum intensity at about 7·4 Å., the whole pattern indicating the poorly crystallized mineral halloysite. The presence of halloysite was also suggested by differential thermal analysis. Montmorillonite is absent from this profile as shown by the glycerol treatment, but vermiculite increases from 1·5 parts in the A horizon to 2 parts in the G_2 horizon. The highest values recorded for illite were found for this profile, ranging from 3 parts in the surface horizon to 5 parts in the G_2 horizon. A small amount of quartz is present, as would be expected for clay separates $< 2\mu$ in diameter. There is a decrease in clay content (40 per cent.–26·4 per cent.) with depth while the C.E.C. of the soils increase from 38·3 m.e. per cent. to 50·5 m.e. per cent. for the A and G_2 horizons respectively. The C.E.C. of the clays increase with depth in agreement with the mineralogical changes.

TABLE I

Mineralogical Composition of the Clay Separates (< 2μ) of Basaltic Soils of Northern Ireland. Results in parts of 10

Profile	*Drainage*	*Horizon*		*Montmorillonite*	*Vermiculite*	*Illite*	*Kaolinite*	*Quartz*	*Feldspar*	*Percentage clay in soil*	*Total exchange capacity of soil (C.E.C. m.e. %)*	*Total exchange capacity of clay separate (m.e. %)*
		Depth (in.)										
Carnanee	Fair to Poor	0–10	A	0	1·5	3	4·5	1	0	40·0	38·3	45·1
		10–20	G_1	..	..	..	..	..	..	34·0	31·8	46·4
		20+	G_2	0	2	5	2·5	0·5	0	26·4	50·5	49·2
Beltoy		0–8	S	0	1	1	7	1	0	40·2	41·2	46·0
		8–16	A–G	0	2	1	7	0	0	40·2	35·6	41·4
		16+	G_2	0	2	1	6	0	1	32·2	43·6	44·4
Ballyno	Poor to Impeded	0–8	A	4	0	1	4	1	0	43·8	49·9	50·8
		8–16	G_1	5	0	1	3	1	0	44·3	47·8	51·2
		16+	G_2	6	0	1	2	0	1	23·9	52·5	47·8
Straidhaven		0–8	A–G	..	..	..	..	..	..	39·1	48·4	..
		8–16	G_1	3	0	0	7	0	0	44·9	40·2	52·5
		16+	G_2	3	0	0	7	0	0	24·3	48·5	58·0
Glynn-Hill		0–10	A–G	0	3	1	6	0	0	40·3	41·5	51·8
		10–15	A–G	1	2	1	5	0	1	43·0	42·1	52·6
		15–20	G_2	3	0	1	5	0	1	40·7	43·6	60·0
Frocess's	Free	0–15	S	0	4	0	6	0	0	27·3	45·3	34·2
		15–24	B_2	0	4	0	6	0	0	21·5	29·8	33·5
		24+	C	..	..	..	..	..	..	11·0	41·2	54·4
Water Commissioners'		0–15	S	0	6	0	4	0	0	26·5	46·5	50·3
		15–30	B_2	0	6	0	4	0	0	16·3	34·8	49·7
		30+	C	0	6	0	4	0	0	10·9	43·0	51·4
Monaghan	Good to Excessive	0–12	S	0	4	1	5	0	0	24·6	46·7	55·8
		12–20	B	0	2	3	5	0	0	21·4	47·7	57·1
		20+	C	0	1	4	5	0	0	11·7	47·3	54·9
Rashee I		0–8	S	0	3	0	7	0	0	32·6	46·3	51·7
		8–15	S	0	3	0	7	0	0	26·5	44·4	52·5
		15–30	B_2	0	3	0	7	0	0	16·6	53·1	50·4
Rashee II		0–8	S	0	3	0	6	1	0	27·3	52·7	42·8
		8–15	S	0	3	0	6	1	0	21·5	54·2	43·3
		15–30	B_2	0	4	0	5	0	1	29·2	55·9	47·5
		30+	C–G	0	5	0	5	0	0	23·3	57·8	48·2

The Beltoy profile, under similar drainage conditions, has much more kaolin, showing similar trends in its distribution, and less illite than the Carnanee profile. Again in this profile the percentage of clay decreases with depth, while there is an increase in the C.E.C. of the soil.

Under the heading of poor or impeded drainage are grouped the three profiles Ballyno, Straidhaven, and Glynn-Hill. The montmorillonite content increases down the Ballyno profile accompanied by a decrease in kaolin, but these changes are not reflected in the C.E.C. values of the clays, which remain relatively uniform. Under impeded drainage the clay separates of the Straidhaven profile show a constant mineralogical composition, kaolin predominating with smaller amounts of montmorillonite, but illite and vermiculite could not be detected in this profile.

Kaolin decreases from 6 parts in the surface horizon to 5 parts in the subsoil horizon of the Glynn-Hill profile. The vermiculite content falls markedly from 3 parts in the surface horizon, disappearing completely below 20 in. where it is replaced by montmorillonite, the amount of which increases with depth. In the field, gleying symptoms were evident in this profile up to the 10 in. mark, and it would appear that vermiculite present in the well-aerated surface horizon gives way to montmorillonite where poorer drainage conditions are found. All three profiles of this series show for the two lowest layers a decrease in clay percentage with depth, yet the C.E.C. values of the soils increase.

The absence of montmorillonite in the two profiles—i.e. Frocess's and Water Commissioners', described as free draining—may be related to the drainage conditions. Considerable amounts of vermiculite are found in both these profiles where the mineralogical compositions are uniform throughout. A striking colour change, which is due to the organic matter and 'free' iron oxides and is not associated with changes in the clay mineralogy (McAleese, 1954), was observed in the Water Commissioners' profile between the S and B_3 horizons. It may be noted that both these profiles show a substantial drop in the C.E.C. value in the B_3 horizon where considerable compaction was encountered.

Grouped on the basis of good drainage are the Monaghan, Rashee I, and Rashee II profiles. Montmorillonite could not be detected in any of these. Corresponding to a decrease in vermiculite with depth in the Monaghan profile there is an increase in the illite content. Whilst the drainage of this profile is described as good there is a slight mottling (possibly due to seasonal wetness) in the lower horizons, and it is possible that under these conditions illite is formed. The smaller amounts in the upper layers may be attributed to the greater degree of weathering. The C.E.C. of the clays are relatively uniform and do not reflect the mineralogical changes.

The mineralogical composition of the clay separates from the Rashee I profile remains constant, as do the rather high C.E.C. values. The good drainage conditions are reflected by the presence of vermiculite. Vermiculite increases in the subsoil horizons of Rashee II, and the C.E.C. values for the clays follow the same trend. There is a general decrease in the percentage of clay in all these profiles with depth and an increase

in the C.E.C. of the soils. However, in Rashee II there is a marked rise in the clay content of the B_2 horizon that may be due to mechanical illuviation.

Considering the profiles as a whole, feldspars are absent from all the surface clays but are found in small amounts for a few subsoil separates. Haematite appears to be the principal form of the iron-oxide minerals with smaller amounts of goethite, but lepidocrocite could not be detected in any of the separates.

The identification of the clay minerals vermiculite and montmorillonite is not always positive because of the possibility of the occurrence of mixed-layer minerals. In the present group of soils where vermiculite is replaced by illite as in the Monaghan profile or by montmorillonite as in the Glynn-Hill profile, the occurrence of mixed-layer structures seems rather probable.

The change in mineralogical composition of the profiles studied can be closely related to the drainage conditions. Kaolin would appear to be the end product of development for the basaltic soils since this mineral is present in greatest amount at the surface where weathering and base depletion are most pronounced. Considering the 2 : 1 minerals, vermiculite predominates under good drainage conditions, i.e. in the groups with 'free' and 'good to excessive' drainage in Table 1, but is gradually replaced by montmorillonite as the degree of waterlogging increases, e.g. Glynn-Hill profile. The basalts are relatively poor in potash feldspars (Kilroe, 1907) and therefore appreciable amounts of illite would not be expected in these soils. With two exceptions (Carnanee and Monaghan profiles) illite is found to be absent or present in only small amounts, but White (1950) and Rolfe and Jeffries (1953) postulate that illites and mica-intermediates weather readily under appropriate conditions into montmorillonites, and the absence of illite in the present group of soils may be accounted for in this fashion.

From the data in Table 1, to explain the increase in the C.E.C. of the soils with depth in the profile, it is evident that material other than clay and organic matter is contributing to the C.E.C. of the soils, and also that the contribution by this material is greatest in the lower, i.e. least weathered, horizons. This aspect will be dealt with in Part V of this series.

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STUDIES ON THE BASALTIC SOILS OF NORTHERN IRELAND

V. CATION-EXCHANGE CAPACITIES AND MINERALOGY OF THE SILT SEPARATES (2–20μ)

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Summary

X-ray and chemical studies of silt separates (2–20μ) from basaltic soils were made to determine the origin of the rather high cation-exchange capacities (C.E.C.) found for these separates. The silts as isolated by the usual method of mechanical analysis consisted in the main of quartz and feldspars with variable amounts of clay minerals which occurred as aggregates. These aggregates were of two types:

(*a*) Composed of clay-size particles, i.e. < 2μ cemented or bound into silt-size aggregates by 'free' sesquioxides of which the basaltic soils have a high content. The aggregates were disrupted by reduction and the clay particles subsequently released.

(*b*) 'Pseudo-aggregates' which were shown to be individual particles of silt-size dimensions and having a flaky appearance. These particles were either vermiculitic (under good drainage conditions) or montmorillonitic (under poor drainage conditions), and it is suggested that they form intermediate products in the weathering of primary-rock minerals to clay minerals.

Whilst the major contributor to the C.E.C. of the silts was undoubtedly the 'pseudo-aggregates' and to a lesser extent the true clay aggregates, most of the silt separates had a much higher C.E.C. than implied by their mineralogical composition.

In the study of the physical and chemical properties of soils, the main emphasis is generally placed on the mineral nature of the colloid fraction, which is regarded as the seat of the physico-chemical activity, e.g. cation exchange. Recent investigations (McConaghy and McAleese, 1957; McAleese and McConaghy, 1957, 1958) show the need to focus attention on the mineral composition of the coarser separates, e.g. silt, in determining the potential fertility level of these soils. These studies have shown that it is not possible to account for the high total cation-exchange capacities (C.E.C.) (of the order 30–50 m.e. per cent.) of the basaltic soils from chemical and mineralogical considerations of the clay separates only (McAleese and Mitchell, 1958). Silt separates as isolated by the ordinary International Method of mechanical analysis are shown to contribute considerably to the total C.E.C. of the soils (McAleese and McConaghy, 1957), and in some cases these contributions are greater than those for the corresponding clay separates.

The present communication records the results of mineralogical and chemical studies of silt separates (2–20μ) in relation to the high C.E.C. of the soils and the contributions by the silts to these values.

Experimental

Silt separates were isolated from the various horizons of ten basaltic soil profiles by the International Method of mechanical analysis, and where modifications were employed, these are described in the text. 'Free' iron oxides were removed from the silts by the sodium-hydrosulphite method (Mackenzie, 1954) and by the Jeffries magnesium-ribbon method (1946). The C.E.C. of the soils were determined by the method of Schollenberger and Simons (1945), and the C.E.C. of the corresponding silts by the micro-distillation procedure of Mackenzie (1952). Specimen preparation and the method of X-ray analysis are as previously described for clays (McAleese and Mitchell, 1958).

Results and Discussion

Estimated amounts of the various minerals present in the silts as determined by X-ray analysis, the percentage of silt, and the C.E.C. of the soils and of the silts are given in Table 1. The figures for the clay contents of the silts given in Table 1 were obtained by difference, i.e. 10–(quartz+feldspars).

The C.E.C. of the soils and the silts increase with depth in the profile and there is also an increase in the percentage of silt. Since the percentage and C.E.C. of the silts increase down the profile, the contribution by this separate to the C.E.C. of the soils will be considerable, especially in the lower horizons (McAleese and McConaghy, 1957). Whilst feldspars (which are considered to have negligible C.E.C.) and quartz make up the greater part of the silts, clay minerals also occur in appreciable amounts, even after reduction with sodium hydrosulphite and subsequent dispersion. The clay minerals (where identification was possible) are mainly montmorillonite and/or vermiculite with smaller amounts of illite and kaolin. However, in the majority of the photographs central blackening prevented positive identification of the clay minerals.

With one exception (Carnanee profile) feldspars are more abundant than quartz in the various profiles, but there is little change in the actual amounts within the profile, as far as could be determined by visual estimation. The presence of clay minerals in the silts readily accounts (at least in part) for the high C.E.C. values found for these separates. In fact observations suggested that in a few of the silts (where the photographs were relatively clear at the centre) there was a greater concentration of the 2:1 clay-mineral type, i.e. the high-exchange minerals, than in the corresponding clay separates. As the basaltic soils have a high content of free sesquioxides (McAleese, 1954) it was reasonable to assume that these exert a considerable cementing action forming silt-sized aggregates from the finer particles. Examination of the corresponding clays (McAleese and Mitchell, 1958) has shown that under poor drainage conditions montmorillonite occurs, and it is possible that this mineral has also binding properties, thus forming aggregates whose dimensions fall within the silt range. Where the drainage conditions were described as good, vermiculite was the dominant 2:1 type of mineral in the clay separates ($< 2\mu$), but this mineral is also found in

TABLE I

Mineralogical Composition of Silt Separates (2–20μ) of Basaltic Soils (Results expressed in parts of 10)

Profile	Soil no.	Drainage	Horizon: Depth (in.)	Horizon	Quartz	Feldspar	Clay*	% Silt in soil	C.E.C. of soil (m.e. %)	C.E.C. of silt (m.e. %)
Carnanee	Z111	Fair to poor	0–10	A	3	3	4	16·9	38·3	14·2
	Z112		10–20	G_1	..	..	..	14·7	31·8	25·0
	Z113		20+	G_2	2	5	3	25·5	50·5	40·2
Beltoy	Z128		0–8	S	1	5	4	17·3	41·2	22·8
	Z129		8–16	A–G	1	5	4	19·4	35·6	25·0
	Z130		16+	G_2	1	5	4	26·6	43·6	41·2
Straidhaven	Z240	Poor to impeded	0–8	A–G	..	..	..	16·0	48·4	..
	Z241		8–16	G_1	2	5	3	16·3	40·2	50·8
	Z242		16+	G_2	1	6	3	31·0	48·5	49·5
Ballyno	Z114		0–8	A	2	6	2	22·1	49·9	35·7
	Z115		8–16	G_1	2	6	2	20·2	47·8	38·6
	Z116		16+	G_2	2	6	2	36·2	52·5	49·5
Glynn-Hill	Z124		0–10	A–G	2	6	2	19·0	41·5	20·5
	Z125		10–15	AG	1	4	5	19·3	42·1	21·6
	Z126		15–20	G_1	2	6	2	27·0	43·6	48·0
	Z127		20+	G_2	..	..	..	31·9	57·1	50·3
Water Commissioners	Z233	Free	10–15	S	1	5	4	22·8	46·5	37·5
	Z234		15–30	B_2	1	5	4	28·4	34·8	38·1
	Z235		30+	C	1	6	3	31·4	43·0	40·4
Frocess	Z246		0–15	S	1	6	3	26·8	45·3	35·9
	Z247		15–24	B_2	1	6	3	20·3	29·8	38·7
	Z248		24+	C	..	..	..	26·8	41·2	47·2
Rashee I	Z117	Good to excessive	0–8	S	1	4	5	27·4	46·3	43·9
	Z118		8–15	S	1	4	5	27·9	44·4	48·3
	Z119		15–30	B_2	1	4	5	28·4	53·1	57·0
	Z120		30+	C–G	..	..	..	29·2	57·0	59·3
Rashee II	Z236		0–8	S	1	6	3	28·8	52·7	39·3
	Z237		8–15	S	1	6	3	31·5	54·3	44·7
	Z238		15–30	B_2	1	6	3	29·5	55·9	46·1
	Z239		30+	C–G	1	6	3	34·5	57·8	51·6
Monaghan	Z243		0–12	S	1	6	3	21·0	46·7	40·9
	Z244		12–20	B	1	6	3	30·3	47·7	48·4
	Z245		20+	C	1	7	2	33·9	40·48	48·0

* The clay values were estimated by difference, i.e. 10–(quartz+feldspar).

many of the silts. However, it is difficult to decide at this stage whether the vermiculite in the silts is in the form of aggregates consisting of clay-size particles or as ultimate silt-size particles.

To determine (1) the contribution to the C.E.C. of the silts by the clay minerals present, and (2) if the latter were aggregates bound by free sesquioxides, six silt separates were subjected to further reduction (three treatments) with sodium hydrosulphite and redispersed with 10 per cent. ammonium hydroxide. The material $< 2\mu$ was then removed, after sedimentation, by siphoning to a particular depth after the appropriate time interval. These processes were repeated until a clear

TABLE 2

The Effect of Repeated Reduction by the Sodium-Hydrosulphite Method and Subsequent Dispersion and Removal of Clay Material ($<2\mu$) on the Cation-Exchange Capacities of Silt Separates ($2–20\mu$)

Silt no.	*Percentage clay in silt*	*C.E.C. of silt before clay removal (m.e. %)*	*C.E.C. of silt after clay removal (m.e. %)*
Z113	14·5	40·5	43·8
Z114	10·5	41·0	33·1
Z115	9·7	39·6	41·7
Z116	7·6	49·9	52·1
Z125	8·3	21·0	23·5
Z235	13·7	60·4	49·7

supernatant was obtained. The C.E.C. values for the silts both before and after the above treatment are given in Table 2 together with the amounts of clay (expressed as a percentage of the silt) removed.

Examination of Table 2 shows that considerable quantities of material $< 2\mu$ can be isolated from the silts after prolonged reduction with sodium hydrosulphite followed by redispersion, and provides ample evidence of the cementing action of the free sesquioxides. However, after clay removal lower C.E.C. values were obtained for only two out of the six silts, which implies that the free sesquioxides were in some way responsible for blocking of the exchange sites. At this stage X-ray examination of the silts showed clay minerals to be still present and apparently unaffected by the reduction procedure employed. The fine material removed from the silts was shown by X-ray analysis to consist of kaolin and, where identification was possible, vermiculite or montmorillonite. However, in the majority of the photographs complete identification of this material ($< 2\mu$) was not possible due to central blackening (in the region where the (001) reflections of the 2:1 clay mineral types occur) which was not the result of scattering of X-rays by the apparatus or specimen support, as shown by other exposures, but may possibly be associated with amorphous material.

In Table 3 results are given for the percentage of silt and the C.E.C. of the silt separates as isolated from basaltic soils (mainly subsoils free from organic matter) by the following methods:

(*a*) Sedimentation and siphoning as in mechanical analysis after usual preliminary pre-treatment, i.e. addition of 0·2 N HCl and dispersion with 10 per cent. ammonium hydroxide, but omitting any oxidative pre-treatment.

(*b*) Sedimentation and siphoning after reduction of the soil with sodium hydrosulphite (three treatments), but omitting oxidation or other preliminary pre-treatment.

(*c*) Part of the silts isolated in (*b*) were then further reduced by the Jeffries magnesium-ribbon method, followed by dispersion and siphoning to remove material $< 2\mu$ (in diameter) released by reduction.

TABLE 3

The Percentage of Silt and the Cation-Exchange Capacities of Silt Separates from Basaltic Soils*

1	2	3	4	5	6	7
Silt no.	*Percentage silt in soil isolated by method (a)*	*C.E.C. of silts isolated by method (a)*	*Percentage silt in soil isolated by method (b)*	*C.E.C. of silts isolated by method (b)*	*C.E.C. of silts isolated by method (b) and further reduced by Mg-ribbon method (c)*	*Percentage clay in silts (b) after further reduction by Mg-ribbon method (c)*
Z113	25·0	40·5	26·9	44·1	39·5	11·1
Z116	36·8	49·9	38·2	54·6	53·8	10·2
Z119	29·1	59·3	30·8	59·4	54·9	7·5
Z127	31·5	47·7	32·0	54·6	45·9	11·4
Z129	19·8	25·3	18·6	28·2	17·3	10·9
Z239	34·4	51·6	32·5	50·3	42·4	11·0
Z242	30·7	49·5	33·1	52·1	46·1	10·2
Z245	35·0	48·0	34·8	50·0	45·5	7·1
Z247	21·2	38·7	24·0	35·6	27·2	9·9

Silts* isolated by:

(*a*) Sedimentation and siphoning after usual preliminary pre-treatment in mechanical analysis, but omitting oxidation with hydrogen peroxide. 10 per cent. NH_4OH used for dispersion.

(*b*) Sedimentation and siphoning after reduction using the sodium-hydrosulphite method, but without oxidation or other pre-treatment.

(*c*) Silts isolated by method (*b*) again reduced by the Jeffries magnesium-ribbon method followed by dispersion, sedimentation, and siphoning.

Method (*a*) was used to determine if oxidative pretreatment before mechanical analysis acting through the free sesquioxides was responsible for the cementing or induration of the clay aggregates present in the silts and thus resisting breakdown to primary-particle size by the procedures used in ordinary mechanical analysis.

The similarity of the results both for the percentage of silt and the C.E.C. of the silts isolated by method (*a*) (Table 3) and those obtained by the ordinary method of mechanical analysis (Table 1) shows that oxidation with 6 per cent. hydrogen peroxide has no effect on the state or amounts of clay aggregates occurring in the silts or on the C.E.C. of these separates.

A higher percentage of silt is found for some of the soils where method (*b*), i.e. reduction with sodium hydrosulphite before dispersion, was employed (Table 3, col. 4). These increases can only be explained by the occurrence of clay or silt aggregates in the fine- and coarse-sand separates which break down to silt size on reduction. The results of Table 2 show that on reduction of isolated silts some clay is released giving a lower percentage of silt, which is sometimes found for the soils

as a whole after reduction with sodium hydrosulphite before mechanical analysis.

Considerable amounts of 'free' sesquioxides were removed from the soils and silts by reduction (McAleese, 1954), indicating that they are partially (at least) responsible for the binding of clay aggregates found in the silts. Seven of the nine silts isolated by method (*b*) gave higher C.E.C. values even when there was an actual decrease in the percentage of silt. The differences may be due to partial blocking of the exchange sites by the 'free' sesquioxides before reduction. X-ray photographs of silts (*b*) revealed that clay minerals were still present and apparently unaffected by the reduction procedure employed. Assuming that all the clay in the silts was in the form of aggregates cemented by 'free' sesquioxides, it was postulated that reduction by the sodium-hydrosulphite method may be too mild in its action to bring about complete disruption of the aggregates.

The silts (*b*) were then subjected to reduction (three treatments) by the Jeffries magnesium-ribbon method (*c*). That this method is more disruptive in its action is shown by the amounts of clay removed (col. 7), but the method may also destroy some of the minerals, as only small amounts of 'free' sesquioxides were released and these amounts would hardly be sufficient to bind the considerable quantities of clay isolated. It is possible that 'free' sesquioxides are not the only binders. The silts (*c*) all gave lower C.E.C. values (col. 6) compared with the silts (*b*) (col. 5), the differences ranging from 0·8 m.e. per 100 g. for silt separate Z116 to 10·9 m.e. per 100 g. for silt separate Z129. However, the C.E.C. of the silts are still remarkably high (17–54 m.e. per cent.) even after removal of the clay. X-ray examination of silts (*c*) showed that clay minerals in the form of 'aggregates' were still present in many of the silts, and persisted even after prolonged reduction by the Jeffries procedure. In some of the silts these 'pseudo-aggregates' had a yellowish-green chloritic appearance under the microscope similar to those found in the fine sands (McAleese, 1954), but in a few cases they were definitely shown to be vermiculitic or montmorillonitic in character, depending on the drainage conditions within the profile.

Mitchell and Muir (1937) directed attention to the high C.E.C. of the coarser separates of certain Scottish soils derived from basic igneous parent material, and the seat of this exchange was related to partially weathered biotitic material. MacEwan (1954) showed that the high exchange in the silts of these Scottish soils was due to polycrystalline aggregates of montmorillonitic character with much greater cell dimensions than normally found for montmorillonoids. Biotite, however, could not be detected in any of the soils of the present investigation. The 'pseudo-aggregates' are undoubtedly single particles occurring in the silts by virtue of their size. They represent an intermediate stage in the weathering of ferromagnesian minerals to vermiculite under good drainage conditions or montmorillonite where the drainage is poor, and are probably polycrystalline pseudomorphs after cleavage fragments of the primary rock minerals, augite and olivine.

Whilst the C.E.C. of the silts can mainly be attributed to the presence

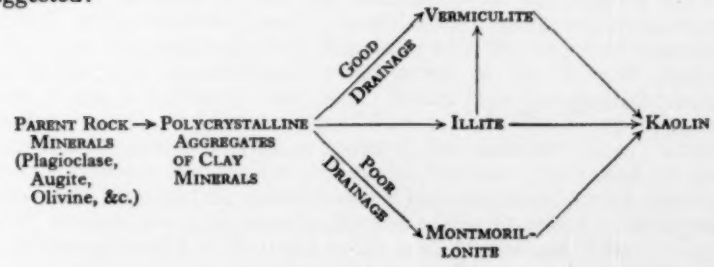
of the so-called 'pseudo-aggregates' with smaller contributions by the true clay aggregates, that for silt separate Z113 is more difficult to explain. The mineral composition of this separate was estimated (from a photograph) to be as follows:

Silt no.	*Quartz*	*Feldspar*	*Illite*	*Kaolin*
Z113	20%	40–50%	25–35%	5%

The photograph was relatively free from central blackening, so that quantities of montmorillonitic or vermiculitic minerals greater than 5 per cent. would be shown on the film. Similarly, mixed-layer minerals would give scattering near the centre of the film and thus be detected. The 10Å. line of illite was fairly sharp, indicating the presence of a normal and quite well-crystallized illite. Material of the composition indicated for silt separate Z113 should have a C.E.C. of about 15 m.e. per 100 g., but the value was approximately 40 m.e. per 100 g.—an excess of 25 m.e.

The difference method used here to estimate the amount of clay in the silts does not allow for the presence of any primary minerals other than quartz and feldspar or for amorphous material and gives, therefore, in this respect a maximum figure. Bearing this in mind and the fact that a small amount of kaolin was detected in most cases, the C.E.C. values for the silts (Table 1) suggest that the aggregates contain a material with a very high exchange capacity ($<$ 120 m.e. per cent. for most of the bottom-layer silts). Although the accuracy of estimating feldspars by powder diffraction is not good and the clay may therefore have been under-estimated, it is not considered that this is a large factor. Another possible explanation is that weathering of the surface of the feldspar grains may have given them a small exchange capacity which would therefore make a significant contribution, since the amount of feldspar is large. However, the most likely explanation is the obvious one, that these stable silt-sized aggregates do in fact have a very high C.E.C.

From the results of Parts IV and V of this investigation the following sequence of weathering for the basaltic soils of Northern Ireland is suggested:



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CHEMICAL STUDIES OF PODZOLIC ILLUVIAL HORIZONS

III. TITRATION CURVES OF ORGANIC-MATTER SUSPENSIONS

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Summary

Titration curves of humus suspensions (prepared from some representative podzol B horizons by acetylacetone extraction) in 0·1 N KCl are presented. The shape of each curve (in absence of added metal ions) and the apparent pK value (pK_e) derived from it are affected by the amount of Al contained in the suspension. One soil extract (initial pH 3·6) had a C/Al ratio of 4·9 and gave pK_e = 6·21, whereas the amberlite-treated extract (initial pH 2·6) had a C/Al ratio of 152 and pK_e = 4·12. Extrapolation of pK_e values to zero concentration of Al gave limiting values of 4·0 and 3·8 for the humus extracted from a Queensland and a New Zealand podzol respectively. These figures are lower than those normally quoted for humic acid, but they may be characteristic of the translocated humus of podzols.

Titration curves of fresh humus extracts with added Al^{+++}, Fe^{+++} or divalent transition metal ions did not suggest the presence of complex sites although the results for Fe^{+++} are uncertain owing to the complexity of the equilibria involved. Similar titrations with added Al^{+++} and Cu^{++} using amberlite-treated extracts did not indicate potential complex sites and, as before, the Fe^{+++} data were inconclusive. By analogy with Cu^{++} it is unlikely that Fe complexes are present in these systems. It is concluded that humus is immobilized in these horizons by electrostatic bonding with Al^{+++} (since free Fe^{+++} would not exist at the soil pH), and the residual Al contained in the organic micelles in suspension is probably also bound by Coulomb forces. It is pointed out that the approximate methods used in this study for practically metal-free preparations may not reveal the presence of the type of complexes found by other workers for some synthetic polyelectrolytes.

MOST current theories on the podzolization process assign a special role to organic matter in the movement of sesquioxides. This hypothesis is attractive because humus accumulations are commonly found in podzol B horizons. Moreover, Bloomfield (1955*a*) in a recent summary of his results suggested that some constituents of certain types of leaf extract are active in mobilizing iron and aluminium in the original parent material. It is postulated that the reactivity of these compounds arises in part from their ability to form complexes with the sesquioxide metals. The mechanism of subsequent precipitation of Fe, Al, and organic matter in the B horizon is less clear. Aarnio (1913) suggested mutual coagulation of Fe and humus sols. Mattson and Nilsson (1935) interpreted the illuviation process in terms of the isoelectric theory which, however, requires that the original profile becomes more alkaline with depth. Deb (1949) did not consider that B horizons were formed either by mutual flocculation of oppositely charged sols or by chemical precipitation of complex salts of Fe and organic acids (Jones and Wilcox, 1929), but suggested that precipitation was controlled by a microbiological process. Gallagher (1942) presented a similar view. Bloomfield (1955*a*)

postulated the adsorption of Fe and Al complexes on to free hydrous oxides and in a recent note (Bloomfield, 1955*b*) suggested that precipitation is related to drying and/or aeration. From preliminary evidence Martin and Reeve (1955) tentatively suggested that Fe, Al, and organic matter were immobilized by complex formation. Studies by other workers using Tamm's acid oxalate reagent, acidic dye absorption (see Russell, 1950, p. 518), and X-ray diffraction data imply the presence of free sesquioxides in the B horizon. Organic matter may therefore have precipitated mainly by mutual flocculation with sesquioxides and may be bonded to them by electrostatic rather than covalent forces. The present studies were designed to show if true complexes occurred in the organic matter isolated from some illuvial podzol horizons. The titration techniques used were based on those described by Beckwith (1955) in a study of complexing sites in the organic fraction of some southern Australian soils.

Experimental

Soil samples. Samples from the humus B horizon of Beerwah sand, Te Kopuru sand, and Glendye 5 soil were used in these experiments. A more detailed description of these soils was given in Part II of this series (Martin and Reeve, 1957).

Extraction. Sufficient air-dry, < 2-mm. soil (generally 10 g.) was extracted for several days with aqueous 0·2 M–0·5 M acetylacetone by the method previously described. After ether extraction and removal of solvent the volume of each suspension was adjusted to give a concentration of organic matter equivalent to about 1 mg. organic carbon per ml. (Walkley-Black titration). All suspensions were kept at 25° C. in presence of a few drops of chloroform, since storage in a refrigerator was found to cause partial flocculation of the organic matter.

Titration procedure. Aliquots of each suspension containing 7–12 mg. C were dispensed into tall 50-ml. Pyrex beakers. Two ml. N KCl and (if necessary) 1–5 ml. metal salt solution were added and the suspension diluted to 20 ml. with distilled water. Additions of 0·05 N NaOH were made from a microburette (reading to 0·02 ml.) the tip of which was immersed in the suspension. Nitrogen gas from a cylinder, presaturated by passing through 0·1 N KCl, was bubbled briskly through each suspension throughout the titration. pH values were determined with a Cambridge pH meter employing a glass electrode—Ag/AgCl/0·1N KCl electrode—immersed in the suspension. Liquid-junction potentials were thus eliminated from the final readings. Duplicate determinations on a few suspensions (both in presence and absence of added metal) showed agreement to within 0·02 pH unit. After each addition of alkali equilibrium below pH 5 was reached in a few seconds. At more alkaline pH values an upward drift occurred which stabilized in 3–5 minutes. At pH 7·5 or greater, readings tended to fall after reaching a plateau value; in one case a decrease of ~0·8 pH unit was observed after standing for 15 days. This decrease was not apparently influenced by the presence of added metal, so that results relating to complex formation

were probably not affected. Drifting was considerably reduced in suspensions that had been almost freed from entrained Al.

Results

Titration curves in the absence of added metal ions. Fig. 1, I illustrates the titration curve obtained from an organic-matter suspension from the

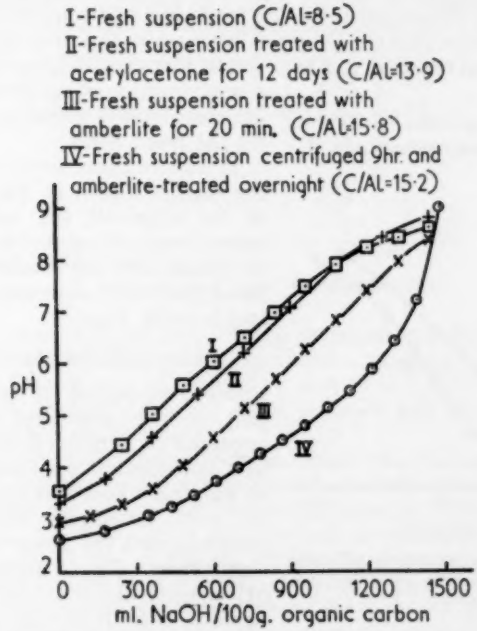

FIG. 1. Effect of C/Al ratio on shape of neutralization curves.

Beerwah groundwater podzol. Curves of similar shape were obtained on suspensions from the Te Kopuru and Glendye soils, and, as found by some workers (Marshall and Patnaik, 1953; Puri and Sarup, 1938), no marked points of inflexion were revealed, although there was in each case a tendency to flatten off at about pH 8. Further treatment of the Beerwah suspension with acetylacetone (0·5 M) for 12 days at pH 4 lowered the Al content by about one-third, reduced the pH of the suspension, and yielded a titration curve (Fig. 1, II) somewhat displaced from the original. When this suspension was passed through a H-saturated cation exchanger (amberlite IR/100) the Al content and pH were further reduced and the resulting curve displaced farther (Fig. 1, III). Since it was later found that amberlite treatment altered the Fe concentration of these suspensions very little it seemed that the shape of the titration curve was directly determined by the Al concentration or,

more specifically, by the C/Al ratio of the preparation. Complete removal of Al from Beerwah and Te Kopuru suspensions was not possible using amberlite alone, but prolonged centrifuging (8 hours at $750 \times g$) followed by overnight mechanical shaking with H-amberlite (using about 300 ml. wet resin per litre suspension) reduced the Al content to very low levels. Fig. 1, IV is a titration curve of Beerwah suspension prepared in this way in which the C/Al ratio has been increased to 152. It has not been possible to remove Al completely from these suspensions even after very prolonged amberlite treatment and centrifuging; further, the ultimate value of the C/Al ratio obtained by this procedure appeared to vary with soil type. It was later found that centrifuging removed only a small fraction of residual Al; amberlite treatment is therefore responsible for the main effect.

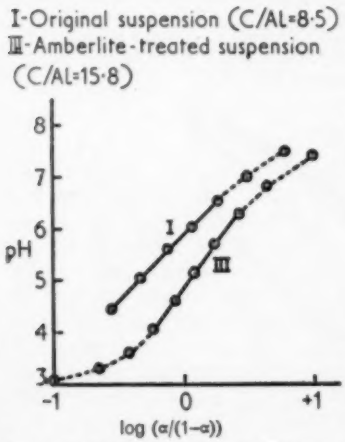

FIG. 2. Relation between pH and $\log(\alpha/(1-\alpha))$ for humus from Beerwah soil.

It is more convenient to summarize the results shown in Fig. 1 in terms of the apparent pK value of each organic-matter preparation. This was obtained from the modified Henderson–Hasselbalch equation (Katchalsky and Spitnik, 1947)

$$\mathrm{pH} = \mathrm{p}K_e + n \log(\alpha/(1-\alpha)),$$

where α = degree of neutralization, $\mathrm{p}K_e$ is the exponent of K_e (the apparent or empirical value for the acid dissociation constant), and n is an empirical constant which is unity for weak monobasic acids but approaches two for some acidic polyelectrolytes. Fig. 2 shows a plot of pH against $\log(\alpha/(1-\alpha))$ taken from curves I and III in Fig. 1. Apparent $\mathrm{p}K$ values were interpolated from the near-linear curves in Fig. 2 at 50 per cent. neutralization; the value for complete neutralization was arbitrarily chosen at pH 8. Table 1 shows the inverse relation between C/Al ratio and $\mathrm{p}K_e$ for humus extracts from the B horizons from Beerwah and Te Kopuru soils. No corrections for ionic strength were made as this was constant at $\mu = 0{\cdot}1$ for each titration; all values are therefore comparable with each other. When $\mathrm{p}K_e$ was plotted against Al/C ratio the limiting $\mathrm{p}K_e$ values (i.e. when Al/C = 0) of 4·0 and 3·8 were obtained for the Beerwah and Te Kopuru preparations respectively.

These results suggest an interference by Al in the titration curves analogous to that in some clay suspensions recently described by Harward and Coleman (1954). It is clear from Fig. 1 that the apparent exchange capacity (to pH 7) increases markedly with decreasing Al content. This is partly due to a greater buffering effect between pH 3·5 and 5·0, but more particularly to the lower initial pH value of the relatively Al-free suspension. Presumably free Al^{+++} ions occupy exchange sites on the

freshly extracted organic matter. The determination of exchange capacity is clearly meaningless on this type of organic matter without the use of metal-free preparations. Assuming that 1 g. C ≡ 2·2 g. organic matter for Beerwah soil, then the exchange capacity (to pH 7·0) for the organic matter in this soil rises from 380 m.e. per cent. for the fresh

TABLE I

Relation Between C/Al Ratio of Podzol Humus to Apparent pK *Value*

Soil	C/Al *ratio*	pK_a
Beerwah Sand . .	4·9•	6·2
	8·4•	5·7
	15·8•	4·8
	152·0†	4·1
Te Kopuru Sand .	3·2•	6·2
	6·5•	5·1
	43·0†	4·0

• Fresh suspensions.
† Suspensions treated with H-amberlite.

suspension to 620 m.e. per cent. for the preparation containing least Al. These values are much higher than those commonly quoted for soil humus (e.g. Russell, p. 276), but they may be a special feature of the more reactive humus extracted from podzols and were, of course, obtained by direct determination.

A characteristic effect shown by fresh humus suspensions used in these experiments was the hysteresis observed on back-titration with acid. Fig. 3, I shows the forward-and-back titrations of Te Kopuru humus (C/Al = 3·2). The two curves are relatively displaced from each other particularly around the midpoints. This effect was also observed by Puri and Sarup (1938) using $Ba(OH)_2$ and H_2SO_4 for the respective titrations; it was attributed by these authors to the presence of $BaSO_4$. From Fig. 3, II it is seen, however, that after treatment of the humus suspension with H-amberlite, the forward-and-back-titration curves were practically contiguous throughout. The Al present in freshly prepared acetylacetone extracts of podzols probably causes the irreversibility of the neutralization curves, and may partly explain the lack of attainment of pH equilibrium at higher pH values.

The Beerwah soil extract showed a similar hysteresis which was also removable by amberlite treatment. On this suspension, several forward-and-back titrations were performed on the same aliquot of suspension. Successive titrations with alkali (or acid) resulted in curves which were displaced farther towards the abscissa and which approached in form the neutralization curve of the amberlite-treated sample. It is possible that repeated changes in pH value occurring during the course of forward-and-back titration could result in a partially irreversible separation of the humus and Al components of the fresh extract, leading to greater accessibility of the true acid sites on the organic-matter molecules.

Titration curves of fresh humus suspensions in presence of added metals. As pointed out by Beckwith (loc. cit.) a consideration of the relative pH drop shown by titration curves of soil organic matter in the presence of transition metals offers the most direct approach to the study of complex compounds in this material. If complex formation between the simple organic ligand (e.g. acetylacetone) and one of these metals (e.g. Cu^{++}) is

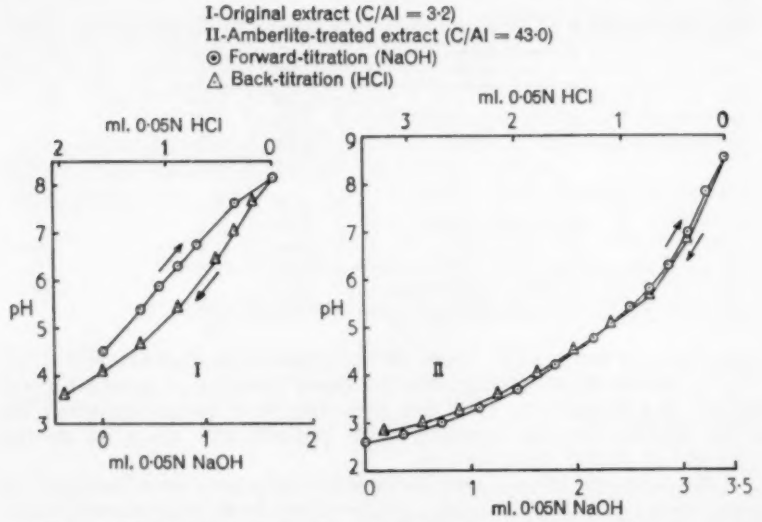

FIG. 3. Effect of amberlite treatment on hysteresis of neutralization curves (Te Kopuru humus).

complete the reaction should yield two equivalents of H^+ per mole of metal over the pH range used in these experiments (4–8·5). Similarly, if a humus suspension is titrated with and without addition of metal ions, the two resultant curves should be separated by an amount of alkali equivalent to the weight of added metal ions if complete complex formation has occurred. However, the titration of transition metal salts alone reveals a consumption of alkali due to formation of the hydroxide or basic salt *above a certain pH value* although this amount of alkali is less than in the presence of a suitable ligand. For example, a solution of $CuSO_4$ titrated alone requires about 1·6 equivalent NaOH per mole Cu^{++} up to pH 8·5. For titrations in systems containing unknown ligands and in absence and presence of Cu^{++} two extreme situations can therefore arise: (i) A release of 1·6 protons per mole added Cu^{++} above about pH 5·8 and persisting at least to pH 8·5 (no complex formation but formation of basic salt), and (ii) a release of 2 protons per mole added Cu^{++} (full complex formation of all added metal). The pH range over which a 2-proton release occurs depends on the stability of the complex but would at least be shown between pH 5 and 8·5. Obviously, inter-

mediate values can be obtained, depending on the relative strengths of the complexes formed.

Another characteristic of complex formation is that the magnitude of the pH drop on adding various transition metals to a ligand solution follows the Irving–Williams stability series (Irving and Williams, 1948) in the absence of steric effects. More explicitly, if separate portions of

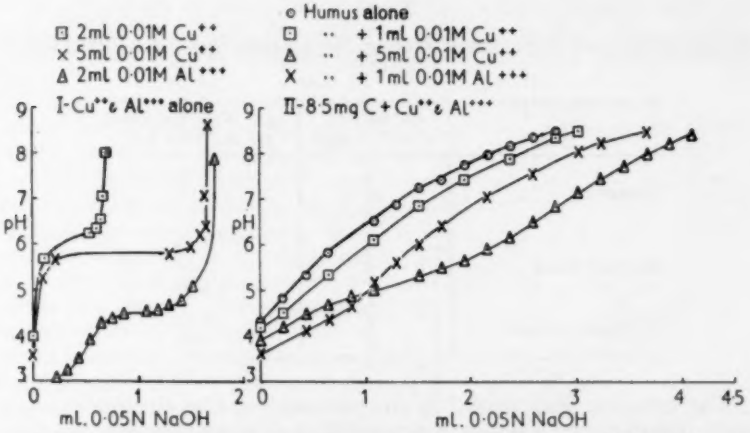
o Humus alone
⊡ 2mL 0·01M Cu++
× 5mL 0·01M Cu++
Δ 2mL 0·01M Al+++
⊡ .. + 1mL 0·01M Cu++
Δ .. + 5mL 0·01M Cu++
X .. + 1mL 0·01M Al+++
I-Cu++ & Al+++ alone
II-8·5mg C + Cu++ & Al+++
pH
mL. 0·05N NaOH
mL. 0·05N NaOH

FIG. 4. Titration curves in presence of Cu and Al (Glendye soil humus).

humus suspensions are titrated in presence of Cu^{++}, Ni^{++}, Mn^{++}, and Co^{++} the relative pH drop compared with the original curve should be in the increasing order $Mn < Co < Ni \ll Cu$.

These two criteria have been applied to the humus suspensions used in the present studies. All titrations were carried out, as previously described, in 0·1 N KCl medium in the presence of nitrogen gas.

Fig. 4 shows the titration curves of a humus suspension from Glendye 5 soil alone and with separate additions of Cu^{++} or Al^{+++}. Also shown are the corresponding curves for the separate titrations of $CuSO_4$ and $AlNH_4(SO_4)_2$ solutions. The horizontal displacement of the Cu curves (after precipitation of the basic salt at pH 5·8–6·2) was equivalent to 1·66 protons per mole Cu^{++}. The proton release on adding Cu^{++} to this humus suspension was 1·2 (for 1 ml. 0·01 M Cu^{++}) and 1·5 (for 5 ml. 0·01M Cu^{++}). The Cu–organic matter curve (5 ml. added $CuSO_4$) shows a point of inflexion corresponding to the pH of precipitation of the basic copper salt and thereafter it is parallel to the no-Cu curve. The point of inflexion on the 0·01 M Cu–organic matter curve is not easily seen but parallelism with the no-Cu curve starts at about the same pH value of 5·7. Neither the full 2-proton release occurred, nor was the precipitation of basic copper salt affected by the presence of freshly extracted humus from the soil, and it is concluded that no complex formation took place. This situation is analogous to that described by

Albert (1950) in comparing the titration curves of copper salts of boric acid and glycine. Similar results were obtained for other B horizon humus extracts, details of which are given in Table 2. None of the preparations gave a proton release greater than that shown by $CuSO_4$ alone and all curves showed evidence of basic salt precipitation in the region of pH 5·8.

TABLE 2

Proton Release on Titration of Humus Suspensions (8·5 mg. C) in Presence of Cu^{++}

Soil	*ml.* 0·01 M $CuSO_4$ *added*	*m.e.* NaOH *required per millimole* Cu^{++}
Glendye 5 . .	8	1·50
	25	1·66
	50	1·61
Beerwah Sand . .	1	1·56
	5	1·61
	8	1·56
Te Kopuru Sand .	1	1·51
	5	1·45

The situation with regard to complexation of iron or aluminium is more complicated. Complete precipitation of the hydroxides of these metals occurs at lower pH values than for the first transition group of metals (~pH 2·3 for $Fe(OH)_3$, 4·8 for $Al(OH)_3$; see Britton, pp. 49 and 66) and since either the formation of 3 : 1 complexes or the hydroxide involves a 3-proton release it is impossible to decide, as in the case of copper, which reaction predominates by inspection of the titration curves (see, however, Schnitzer and DeLong, 1955). Moreover, it is likely in the case of Fe that several ionic species participate in a number of stepwise reactions involving Fe^{+++}, $Fe(OH)_2^+$, and probably dimeric forms at pH 2–3 (Mulay and Selwood, 1955). Similar considerations apply to Al (Brosset, 1952). There is thus some uncertainty as to the equilibria involved and it is impossible to use spectrophotometric procedures (at least in the visible range) on soil organic matter owing to the flocculating action of these metals. There seems to be no satisfactory way at present of deciding on the type of bond existing between these metals and the humus of the podzol B horizon. From Fig. 4, II the titration curve of Glendye humus in presence of Al shows a relatively sharp change in direction at pH 4·7; thereafter the curve exactly parallels the original titration curve in absence of added metals. At this pH it is seen from the Al curve in Fig. 4, I, that precipitation of the hydroxide is practically complete. It is reasonable to assume, therefore, that the presence of organic matter has no influence on precipitation of the hydroxide of added Al and that the metal is not complexed. Titrations of ferric chloride solution (initial pH 1·6) show no points of inflexion corresponding to precipitation of the hydroxide, neither do ferric

chloride–humus mixtures, so that no firm conclusion can be drawn with respect to the bonding of Fe^{+++} to organic matter by this technique.

Order of pH drop on addition of various metal ions. Titration curves of fresh Te Kopuru suspension alone and in presence of 2 ml. 0·01 M solutions of some metal salts are shown in Fig. 5. Copper gives the greatest displacement, nickel the least. The curves of Ni, Co, Mn, and Zn are indistinguishable below pH 5·5, but at pH 6·5 the order of pH reduction is $Ni < Mn < Co \ll Cu > Zn$ compared with the Irving–Williams series $Mn < Co < Ni \ll Cu > Zn$. For similar curves from the fresh Beerwah preparations the order at pH 6·5 was $Mn < Ni < Co \ll Cu$. Thus in both soil extracts the positions of Co and Ni were reversed and in the Te Kopuru sample Mn occupied an anomalous position. Beckwith's data (loc. cit.) show curves for Co, Ni, and Mn that are located relatively close together, but the Irving–Williams order was distinctly preserved. In particular, the Cu curve obtained by this worker showed a drop of approximately three pH units at one point compared with that from the original humus preparation, strongly indicating complex formation. This is not shown for the podzol humus extracts examined in this study.

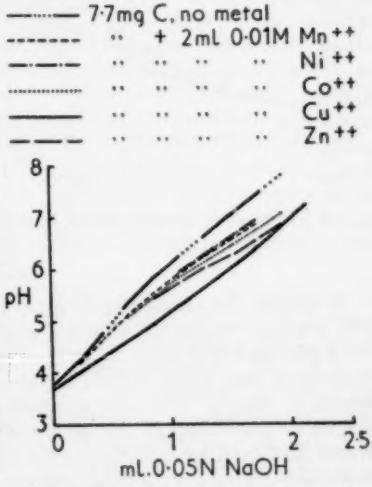

FIG. 5. Titration of Te Kopuru soil humus in presence of metals.

Titration curves of amberlite-treated suspensions. The effects of added Cu^{++} and Al^{+++} on the titration curve of Te Kopuru humus suspension that had been shaken overnight with H-amberlite and centrifuged are shown in Fig. 6, I. Corresponding curves for the amberlite-treated Beerwah suspension were of similar shape, and it is seen that these preparations show titration data which differ from that on fresh acetylacetone extracts in two ways: (i) There are no regions where the precipitation of either metal hydroxide can be recognized, although it is not certain how much the comparatively strong buffering effect of each preparation would mask this, and (ii) the relative displacements for the original curve increase with rise in pH but are at all points considerably less than those of fresh soil extracts. A plot of pH against $\log\{\alpha/(1-\alpha)\}$ for the original and Cu^{++}-treated suspensions are shown in Fig. 6, II. The curves are particularly contiguous and are for the most part linear. This, according to Gregor *et al.* (1955), implies the absence of any specific effect between Cu^{++} and the humus polyanion. Similar relations were obtained with an Al^{+++}-treated suspension. Titrations in presence of Fe^{+++} were complicated by the presence of excess mineral acid (added to ensure maximal concentrations of free ferric ions) and the derived curve (pH *v.* $\log\{\alpha/(1-\alpha)\}$)

fluctuated about a mean axis roughly corresponding to that of the original. No satisfactory conclusion could be formed with regard to complexation with Fe^{+++}.

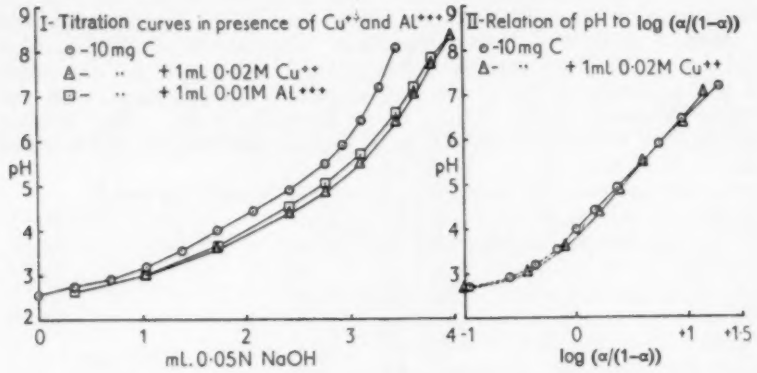
I- Titration curves in presence of Cu++ and Al+++
o -10 mg C
Δ - " + 1 mL 0·02M Cu++
□ - " + 1 mL 0·01M Al+++
pH
mL. 0·05N NaOH
II-Relation of pH to log (α/(1-α))
o -10 mg C
Δ - " + 1 mL 0·02M Cu++
pH
log (α/(1-α))

FIG. 6. Titration curves of amberlite-treated Te Kopuru humus.

Discussion

It should be emphasized again that the values reported for apparent pK are only approximations and neglect the well recognized influences of ionic strength and degree of neutralization on the dissociation of hydrogen ions from colloidal polyacids (Speiser, 1947; Katchalsky and Spitnik, 1947). For our purpose it is sufficient to indicate that the apparent pK values of our preparations were lower by 1·3–2·2 units than those obtained by other workers for humic acid. Dawson *et al.* (1950) reported pK = 5·2 for acid-washed wood peat neutralized with $Ca(OH)_2$. Interpolated results from the published curves of Marshall and Patnaik (1953), Gillam (1940), and Puri and Sarup (1938) yield apparent pK values (in absence of neutral electrolyte) of 5·4–6·1 for humic acid. These may be contrasted with the average extrapolated value of 3·9 found from our results with humus preparations of low Al content in 0·1N KCl. This difference in pK may (as previously suggested in connexion with exchange capacity) reflect real differences between the constitution and properties of illuvial podzol humus and 'humic acid' derived from more alkaline soils. There is some evidence in the literature that the B_h podzol organic matter is largely composed of the so-called 'fulvic acid' fraction (Ponomareva, 1949; Kosaka and Honda, 1955) and the exchange capacity of 'fulvic acid' has been reported to be relatively high (Ponomareva, 1947, quotes 620 m.e. per cent.). The results reported in this paper are in accord with these findings and suggest that the amberlite-treated suspensions were essentially similar to the sols of 'fulvic acid' described by other workers.

Titration curves of the fresh humus extracts in presence of metals showed no evidence of complex formation with Al or the divalent transi-

tion metals used. The results for Fe were inconclusive, but by analogy with the Cu results the presence of surface Fe complexes is probably unlikely. If so, the humus in the B horizon of these podzols is rendered immobile by essentially electrostatic bonding or mutual coagulation, and not complex formation.

The status of the residual metals entrained in the fresh extracts is not so clear. From the sedimentation tests reported in Part II (Martin and Reeve, 1957) of this series it was suggested that some of the entrained Al was physically distinct from the organic fraction. This was more evident in the Te Kopuru soil, which contains kaolinite. Ash determinations were not performed on the fresh extracts; it is thus possible that kaolinite was present in sufficient quantity to interfere with the titration curves of the Te Kopuru preparation, but their close similarity to the curves of the fresh Beerwah extract (this soil contains virtually no clay minerals) suggests only minor interference from this source. Because of this, and the fact that amberlite treatment is relatively effective in removing most of the Al, it is probable that the bulk of the metal present in fresh humus extracts of these soils occurs on surface organic sites which are readily accessible to the exchanger. Acetylacetone is not efficient in removing residual Al, no doubt because the low pH values developed as Al is progressively removed result in instability of the Al-acetylacetone complex.

The titration curves of amberlite-treated humus, in presence of metals, do not suggest that the residual Al is complexed, but there must be some uncertainty as to the nature of the bond between metal ions and the sites opened up by treatment with a cation exchanger. Recent work on the Cu complexes of polyacrylic and polymethacrylic acids by Gregor *et al.* (1955), using titration curves and a modified Bjerrum treatment for calculating stability constants, suggests the formation of Cu complexes containing eight-membered rings which are stabilized by the electrostatic effects of the large polyelectrolyte coil. In a recent note, Coleman, McClung, and Moore (1956) report the use of similar methods in a study of the Cu complexes of acid-washed peat and postulate that, in this material, conditions with respect to the binding of metal ions are similar to those operating in synthetic polyelectrolytes. If this concept is correct, the detailed aspects of metal ion–humus bonding cannot be studied in terms of the formation of simple, bidentate complexes since steric factors and electrostatic properties exert marked effects on the character of the association. If some kind of electrostatic bonding is involved in podzol humus it would probably exclude Fe from direct flocculation of the organic matter since free ferric ions would not exist at the reaction (pH 4·2–4·6) of these samples.

Acknowledgements

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FACTORS AFFECTING THE ABILITY OF PLANTS TO ABSORB PHOSPHATE FROM SOIL

II. A COMPARISON OF THE ABILITY OF DIFFERENT SPECIES TO ABSORB LABILE SOIL PHOSPHATE

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Summary

Barley, rye, and cabbage have been used as test plants to measure labile soil phosphate by the Larsen procedure. In some soils higher values are given by rye and cabbage than by barley. These differences are believed to reflect the greater ability of cabbage and rye to lower the free energy of phosphate in the external medium. Thus, in soils containing large quantities of labile phosphate at a low potential, sources of phosphate that are inaccessible to barley are accessible to the other two species.

Introduction

THE entry of ions into the roots of plants is a complex physiological process, the rate of which is greatly influenced by many environmental factors. However, plant-physiological considerations are frequently ignored in discussions of factors affecting the absorption of nutrients by plants grown in the soil, and interpretations are sought mainly if not exclusively in terms of soil chemistry. Inter-specific differences in the extent to which different species absorb phosphate are well known, but there is little evidence to show whether they are due to some forms of phosphate in soils being accessible to some species only or whether species differ merely in the rates at which they can absorb from a common source. To provide information on this question the Larsen (*L*) values obtained with different test plants were compared in two experiments described in the preceding paper of this series (Russell *et al.*, 1957). Additional information was obtained in water-culture experiments which were carried out by the methods outlined by Russell and Martin (1953). Barley, rye, and cabbage were selected as test plants since barley is reputedly of low efficiency in absorbing phosphate from acid soils, whereas the latter two absorb considerably greater quantities.

Experimental Results

Comparison of barley and cabbage. Cabbage (Wheeler's Imperial) and barley (Proctor) were grown for 70 days in an acidic basalt soil (soil IV) which had been enriched with unlabelled phosphate to the following levels: 1·5, 2·8, 6·0, 9·0 mg. P per 5 g. soil (Russell *et al.*, 1957, Experiment 6). The results of the comparison of species are summarized in Table 1: data for barley grown in soils enriched with 1·5 mg. P

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TABLE I

Plant Yield, Absorption of Phosphate and L *Values obtained by Growing Cabbage and Barley in Soil IV for 70 days*

Soil treatment (*mg.* P/5*g. soil*)	*Dry weight* (*mg./pot containing 200 g. soil*)		*Absorption of phosphate* (*mg.* P/5*g. soil*)		L *value* (*mg.* P/5*g. soil*)		E *value* (*mg.* P/5*g. soil*)
	Cabbage	*Barley*	*Cabbage*	*Barley*	*Cabbage*	*Barley*	
1·5	907	..	0·020	..	2·01	..	2·92
2·8	1,317	1,849	0·050	0·082	3·31	2·64	3·67
			(0·70)	(0·91)	(1·52)	(1·42)	..
6·0	2,188	1,849	0·144	0·088	6·50	4·55	5·79
			(1·16)	(0·94)	(1·81)	(1·66)	..
9·0	1,987	1,341	0·191	0·089	8·94	6·18	7·71
			(1·28)	(0·95)	(1·95)	(1·79)	..
S.D. (P = 0·05)	266		(0·13)		(0·05)		0·31

1. When data were analysed statistically on a logarithmic basis the transformed values are shown in brackets.

2. Results for soil enriched with 1·5 mg. P were excluded from statistical analysis since absorption by barley from this soil was too low for accurate determination.

Analysis of Variance

	Statistical significance (P)		
	Yield	*Absorption of phosphate*	L *value*
Soil treatment . . .	0·001	0·001	0·001
Crop	0·001	0·001	0·001
Soil treatment × crop . .	0·001	0·001	0·01

are excluded because the absorption of phosphate was too low for accurate determination. Values for isotopically exchangeable phosphate, *E*, obtained after a 7-day equilibration period are also shown. The two species gave significantly different *L* values. In Fig. 1 it is shown that the *L* values for each species bore a closely linear relation to the quantity of phosphate added to the soil, *T*. The coefficient of the linear regression of *L* (cabbage) *v.* *T* is not significantly different from 1, while that for *L* (barley) *v.* *T* is in the order of 0·6, which is similar to the regression coefficient for *E* *v.* *T*. Thus the regression coefficient for *L* (cabbage) *v.* *E* exceeded 1 to a significant extent while that for *L* (barley) *v.* *E* was not significantly different from 1 (Fig. 2). These results indicate that all the phosphate added to the soil had contributed to the *L* (cabbage) value. Some mechanism in the soil, however, restrained approximately one-third of the added phosphate to such an extent that it was inaccessible to barley and was moreover not isotopically exchangeable in the seven-day equilibration period employed to determine *E*.

Comparison of barley and rye. Barley and rye were compared in soil I, a calcareous alluvium, and in soils III and IV which were both basaltic. The soils had been enriched with 1·5 mg. P per 5 g.; in addition soil I was used without added phosphate. Absorption from the other two

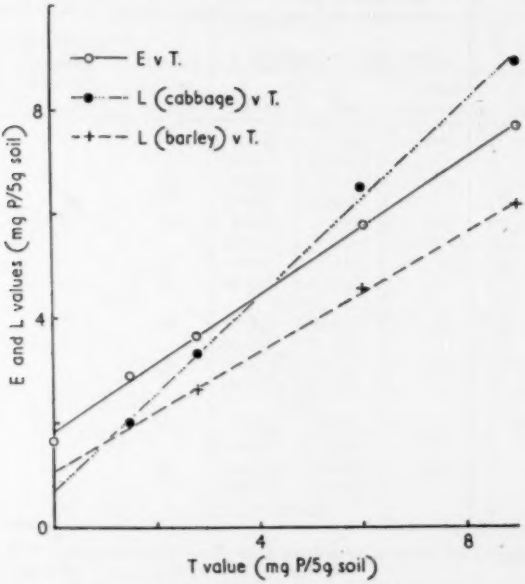

FIG. 1. The relationship between labile soil phosphate and the quantity of phosphate (*T*) added to soil IV. Labile soil phosphate was measured as exchangeable soil phosphate (*E*) and by the Larsen procedure (*L* value), with cabbage and barley as alternative test plants.

Regression equations:

$$E = (0{\cdot}66 \pm 0{\cdot}03)T + 1{\cdot}79.$$
$$L \text{ (cabbage)} = (0{\cdot}93 \pm 0{\cdot}07)T + 0{\cdot}70.$$
$$L \text{ (barley)} = (0{\cdot}57 \pm 0{\cdot}13)T + 1{\cdot}07.$$

soils was too low for *L* values to be determined until phosphate had been added (Russell *et al.*, 1957, Experiment 7). The results for plants sampled after two periods of growth, namely 28 and 56 days, are shown in Table 2. Only small changes in *L* value occurred between the two sampling occasions. In soil I and also in soil III both species gave the same *L* values, but in soil IV the value for rye was approximately twice as great as that for barley. This effect was highly significant statistically. The ratios of the absorption of rye to that of barley are shown in Table 2. After a growth period of 28 days striking differences were apparent, the ratio being highest in soil IV from which the plants derived least phosphate, and lowest in soil I enriched with 1·5 mg. P per 5 g. from which the quantity of phosphate absorbed was greatest.

Between 28 and 56 days the relative magnitude of the absorption of

the two species changed considerably in soil IV; the phosphate content of barley increased by a factor of nearly 13 between the two sampling occasions, while the corresponding factor for rye was less than 2. At the second harvesting occasion the two species were in contrasting phases of

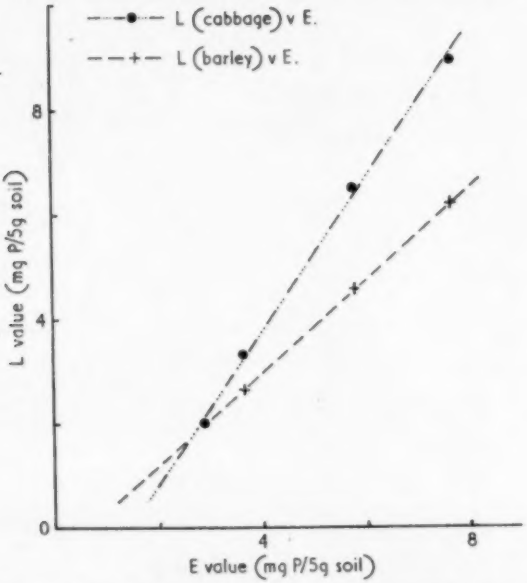

FIG. 2. The relationship between Larsen value as determined with barley and cabbage as alternative test plants and exchangeable soil phosphate (E) in soil IV

Regression equations:

$$L \text{ (cabbage)} = (1.45 \pm 0.11)E - 2.07.$$
$$L \text{ (barley)} = (0.88 \pm 0.22)E - 0.56.$$

growth; barley was still tillering while in rye tillering had ceased and the tillers were commencing to elongate. For this reason the relative extent of absorption in the two crops between the two sampling occasions must be expected to have reflected factors other than interspecific differences in ability to absorb different forms of soil phosphate. None the less, as has already been noted, each species showed a constant L value throughout the experiment, that for rye being approximately twice that for barley.

The results for the first sampling occasion in this experiment suggest that barley is initially markedly less effective at absorbing phosphate than rye when the external supply is low. This question was further examined in water-culture. Barley and rye plants which had been grown to the second-leaf stage without external supplies of phosphate but with ample levels of other nutrients were treated for 4 hours with concentrations of labelled phosphate ranging from 10 to 0·001 p.p.m. P. This

TABLE 2

Absorption of Phosphate and L *Values Obtained with Barley and Rye Grown in Different Soils*

(Results expressed as mg. P/5g. soil)

Soil no.	*Quantity of phosphate added (mg. P/5 g. soil)*	*Growth period (days)*	*Absorption of phosphate*			L *value*	
			Barley	*Rye*	*Ratio rye/barley*	*Barley*	*Rye*
I	1·5	28	0·175 (2·24)	0·175 (2·24)	1·0	1·82	1·80
	..	56	0·309 (2·49)	0·316 (2·50)	1·0	1·87	1·86
II	nil	28	0·040 (1·60)	0·054 (1·73)	1·3	0·50	0·49
	..	56	0·098 (1·99)	0·108 (2·03)	1·1	0·59	0·59
	S.D.		(0·07)		..	0·08	
III	1·5	28	0·031 (1·49)	0·058 (1·76)	1·9	1·63	1·74
	..	56	0·075 (1·88)	0·131 (2·12)	1·7	1·79	1·84
	S.D.		(0·07)		..	0·14	
IV	1·5	28	0·0057 (0·76)	0·031 (1·49)	5·4	0·94	1·80
	..	56	0·073 (1·86)	0·058 (1·76)	0·8	0·96	1·86
	S.D.		(0·08)		..	0·16	

When data were analysed statistically on a logarithmic basis the transformed values are shown in brackets.

short treatment period was employed so that the relative ability of plants of *equal phosphate status* to absorb from solutions of different concentrations could be compared. Complications due to modifications in growth form such as those observed at the second sampling occasion in the preceding experiment could thus be avoided. Since a constant activity of labelled phosphate was used per unit volume of solution in all treatments it is convenient to express the results (Table 3) in terms of ^{32}P absorbed. Differences in this quantity reflect differences in the percentages of phosphate in the treatment solutions which entered the plants. The values for rye increased progressively with decreasing external concentration: with barley by contrast the maximum value occurred when the concentration of the external solution was 0·01 p.p.m. P—the decrease at the lowest concentration accords with previous observations (Russell and Martin, 1953). An analysis of variance showed that the interaction of species with respect to absorption was highly significant ($P < 0·001$). The nature of this interaction is most readily shown by the ratio of the absorption of rye relative to barley. The magnitude of this ratio (Table 3) was inversely related to the external concentration. Further evidence is therefore provided that rye has a greater ability than barley to absorb phosphate when the external supply is limited.

TABLE 3

Absorption of Phosphate by Young Rye and Barley Plants treated for 4 hours with Varying Concentrations of Phosphate

(A constant activity of ^{32}P was used per litre of culture medium, and the results can therefore be expressed in terms of the ^{32}P absorbed)

Concentration of phosphate (*p.p.m.* P)	mμc ^{32}P/*plant*		*Ratio rye/barley*
	Rye	*Barley*	
10·0	166	200	0·83
1·0	290	326	0·89
0·1	443	561	0·79
0·01	735	669	1·10
0·001	763	597	1·28
S.D. (P = 0·05)	83		..

Analysis of Variance

	Statistical significance (P)
Concentration of phosphate .	0·001
Crop	Not significant
Concentration × crop . .	0·001

Discussion

The manner in which the Larsen value is determined has been discussed in the first paper of this series (Russell *et al.*, 1957). Its magnitude depends on the extent to which ^{32}P added to the soil is effectively diluted on absorption by plants; it is independent of the quantity absorbed. The difference in *L* value observed between barley and both cabbage and rye grown in soil IV therefore reflects the fact that the specific activity of phosphate (i.e. $^{32}P/^{31}P$) was not constant throughout the labile soil fractions which the plants absorbed. Two causes could lead to this situation:

(i) Non-uniform initial incorporation of ^{32}P in the soil.
(ii) Physico-chemical differences between labile soil phosphate fractions which are of sufficient magnitude to prevent a constant specific activity being attained throughout the phosphate which plants absorb.

If non-uniform incorporation of ^{32}P were responsible for differences in specific activity, contrasting *L* values could result from interspecific differences in the spatial distribution of the roots. If, however, physico-chemical differences are the sole cause of the variations in the specific activity of the labile soil phosphate, differences in *L* value would indicate that part of the labile phosphate in the soil is accessible to one species but not to another.

Gross differences in the distribution of ^{32}P in the soil were prevented by the mixing procedures employed in the present experiments (Russell *et al.*, 1957). The possibility of non-uniform distribution on a micro-scale cannot, however, be excluded. For example, it might be postulated

that differences in the positions in which ^{32}P was adsorbed on individual soil crumbs might make it differentially accessible to species which contrast in the morphology of their roots. If this occurred, increasing absorption by plants would deplete the sites of preferential adsorption and in consequence the differences between species would be expected to be reduced with time. The occurrence of isotopic exchange in the soil would have a similar effect. Furthermore the nature of interspecific differences would be expected to be greatly modified if the soil were enriched with varying levels of ^{31}P prior to the addition of ^{32}P. The present experiments provide evidence that interspecific differences in L value are constant with time and that they are unaffected by the prior enrichment of the soil with phosphate.

These findings indicate that non-uniform mixing of ^{32}P in the soil cannot explain the contrasting L values; an explanation must therefore be sought in terms of physico-chemical differences between different labile phosphate fractions. The extent of such differences is indicated by the fact that rapid and slow exchange reactions can readily be distinguished in soil (McAuliffe *et al.*, 1948; Russell *et al.*, 1954). Until isotopic equilibrium is fully attained—a process which may take several weeks—the more slowly exchangeable fractions will be the lowest specific activities. The high values for rye and cabbage relative to barley in soil IV therefore suggest that slowly exchangeable phosphate fractions were more accessible to rye and cabbage than to barley. A possible explanation of this situation may now be considered.

Since very intimate contact occurs between the external surface of roots and the soil, and since the migration of phosphate in the soil is slow, it is envisaged that when plant roots are absorbing phosphate the equilibration of phosphate between sites in the soil at which it is held with widely differing activation energies is so slight that the plant may be regarded as in contact with a number of *independent* systems of labile phosphate. The free energy of phosphate will differ between these systems. Under the conditions of the present experiments the systems of highest free energy will be those in which equilibration with the added labelled phosphate was most rapid and which therefore showed the highest specific activity. The absorption of phosphate by plants must depend on root surfaces reducing the free energy of the entering ions to a greater extent than complexes with which they would be otherwise associated; thus the higher L values (i.e. lower specific activities of absorbed phosphate) found with rye and cabbage than with barley in soil IV indicate that barley was unable to lower the free energy of phosphate to the same extent as cabbage or rye, and that labile phosphate systems of low free energy (and low specific activity) were consequently accessible only to the latter two species. The greater ability of rye than barley to absorb phosphate from very dilute solutions can be similarly explained.

Interspecific differences arising in this way would be expected to be marked only in soils containing significant quantities of labile phosphate the free energy of which is too low for one species to absorb it. In view of the fact that rye and barley showed contrasting L values in soil IV

but not in soils I and III it is of interest to examine the characteristics of these soils:

	Soil I Calcareous alluvium	*Soil III Basaltic*	*Soil IV Basaltic*	*S.D.* (P = 0·05)
Isotopically exchangeable phosphate	0·48	0·75	1·35	0·14
Phosphate sorption . . .	2·40	7·84	8·75	0·06

Isotopically exchangeable phosphate is an index of the quantity of labile phosphate in the system, while sorption is inversely related to phosphate 'potential'. Soil IV, therefore, contrasted with soils I and III in containing larger quantities of labile phosphate at a low 'potential' or free energy level. It is suggested that this is the reason why the *L* values for the two species differed only in soil IV.

As an alternative explanation of these results, it could be suggested that cabbage and rye raised the free energy of the slowly exchangeable phosphate fractions and therefore made them more accessible to plants. Such an effect might be attributed to the absorption of calcium or other cations with which phosphate is associated in the soil. This interpretation is, however, not acceptable since, for reasons previously discussed (Russell *et al.*, 1957), *L* values did not change in consequence of growth and absorption by plants.

The preliminary nature of the present investigation is to be emphasized. None the less it may be regarded as establishing the occurrence of interspecific difference with regard to the *source* from which plants can absorb phosphate and as demonstrating a procedure whereby such a relationship can be explored.

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SOIL PHOSPHORUS FRACTIONS IN SOME REPRESENTATIVE SOILS[1]

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Summary

The distribution of soil inorganic phosphorus in soils was found to measure the degree of chemical weathering, the chemical weathering sequence being calcium phosphate, aluminium phosphate, iron phosphate, and occluded phosphate. The latter category includes reductant soluble iron phosphate and aluminium-iron phosphate occluded in iron oxides. For example, three horizons of one Chernozem profile, a Dark Brown soil, and the calcareous C_1 horizon of a Grey-Brown Podzolic soil contained 68–95 per cent. of their inorganic phosphorus in the form of calcium phosphate, the other forms decreasing exponentially in the sequence. The inorganic phosphorus of two Latosols increased exponentially in the order calcium phosphate (1%), aluminium phosphate (0–3%), iron phosphate (10–13%), and occluded (reductant soluble) phosphate (66–78%). Three samples of podzolized soils contained intermediate, sigmoidal distributions of the four phosphates.

In two Miami silt loam profiles, the 0·002 N H_2SO_4-extractable-phosphorus test was much higher in the subsoils down to 3½ ft. than in the surface soil, and was correlated mostly with the calcium-phosphate content, somewhat with aluminium and iron phosphate, and none at all with occluded phosphates which constituted a high percentage of the total phosphorus. The higher content of available phosphorus in the subsoils and release of phosphorus in the surface soil by decrease of Al and Fe activity through liming most probably explain the lack of crop response to added phosphate fertilizer even though the surface soil had a low phosphorus test.

Application of phosphate fertilizer to Almena silt loam greatly increased the amount of aluminium and iron phosphate at three lime levels; only a slight increase of calcium phosphate occurred, at the highest lime level. The amount of occluded phosphate remained unchanged by liming or fertilization. The relatively small increase of calcium phosphate through phosphate application is attributable partly to crop removal but is shown to be due mostly to formation of the less soluble iron and aluminium phosphates.

WHILE extensive studies have been made on the total as well as available amount of phosphorus in the soil, little work has been done on the distribution of various discrete chemical forms of inorganic phosphorus in the soil, owing to incompleteness of methods. Knowledge of the specific chemical forms of inorganic phosphates is, however, important in understanding the chemistry of soil phosphorus and also has importance to soil genesis and soil fertility. The distribution of various forms of inorganic phosphorus in the soil is no doubt controlled by the activities of the various ions in the soil, in turn reflecting soil pH, age, drainage, and mineralogical nature. Fractionation of soil phosphorus also permits

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tracing the fate of applied phosphate fertilizer under different soil conditions. Since the various forms of phosphates have different solubilities, their distribution might give an indication about the availability of phosphorus in the soil, although the latter is largely determined by the amount of surface of the various forms.

Literature Review

By use of pH variable-phosphate-solubility curves, the forms of soil phosphorus have been studied qualitatively in Arizona soils (McGeorge and Breazeale, 1932), in South Wales soils (Holman, 1937), in Colorado soils (Gardner and Kelley, 1940), and in the C horizons of Iowa soils (Stelly and Pierre, 1942). Allaway and Rhoades (1951) studied the distribution of NH_4F-extractable phosphorus in the horizons of several Nebraska soils. Bauwin and Tyner (1954) studied the distribution of NH_4F-extractable and reductant-extractable soil phosphorus in several major soil groups. Dean (1938) fractionated into solubility classes the phosphorus of thirty-four soil samples from locations in Africa, Great Britain, Hawaii, Russia, and the United States. He also studied the fate of applied phosphate fertilizer on Rothamsted and Woburn farm soils. Ghani (1943) improved that method of fractionation of soil phosphorus and studied the distribution of various forms of phosphorus in twenty Indian soils. Williams (1950*a*, 1950*b*) further improved the method and studied the forms of soil phosphorus in South Australia soils and their relation to soil fertility. These methods do not differentiate aluminium phosphate from iron phosphate as was done in the present study by a more complete method (Chang and Jackson, 1957*a*). Ghani and Williams employed an acid extraction before alkali extraction and, therefore, may not have obtained a complete separation of calcium phosphate from the iron and aluminium phosphates.

Materials and Methods

In this investigation the soil phosphorus in several widely different soil types was fractionated according to the method of Chang and Jackson (1957*a*) into aluminium phosphate, iron phosphate, calcium phosphate, reductant soluble iron phosphate, and occluded aluminium-iron phosphate (barrandite-like). Aluminium phosphate is extracted at room temperature with neutral 0·5 N NH_4F. Iron phosphate is subsequently subtracted from the same sample with 0·1 N NaOH at room temperature. Calcium phosphate is extracted with 0·5 N H_2SO_4 at room temperature. Reductant soluble (occluded) iron phosphate is next extracted by means of citrate-dithionite reagent ordinarily used for the removal of extractable free iron oxides of soils (Aguilera and Jackson, 1953). After this the occluded aluminium phosphate is extracted, as ordinary aluminium phosphate was previously. The presence of occluded aluminium-iron phosphate (barrandite-like) is established by these relationships: the dithionite treatment dissolves iron phosphate but not aluminium phosphate; more phosphate is dissolved in NaOH than NH_4F following the dithionite treatment; therefore, aluminium

phosphate apparently occludes some iron phosphate in barrandite-like form. The discreteness and reliability (within approximately the colorimeter error) of measurement of the various specific chemical forms of phosphate is established in the original publication (Chang and Jackson, 1957*a*). In a few samples, the organic phosphorus was also determined according to the method of Bray and Kurtz (1945).

The first set of samples includes ten soils representing some widely different major soil groups:

1. Wahiawa clay loam, lower A horizon, 10–18 in., a dark reddish-brown Low Humic Latosol, with 10·1 per cent. extractable Fe_2O_3, pH 6·7, and layer silicate clay largely halloysite.
2. Catalina A horizon, 12–36 in., a Latosol (probably a Low Humic Latosol) from Puerto Rico, with 18·2 per cent. extractable Fe_2O_3 and pH 6·7.
3. Miami silt loam, A_3 horizon, 12–16 in., a virgin Gray-Brown Podzolic soil from Dane County, Wisconsin, with 1·4 per cent. extractable Fe_2O_3, pH 5·8, and layer silicate clay largely montmorillonite.
4. Miami silt loam, C_1 horizon, 46–58 in., from the same profile as 3, with 1·2 per cent. extractable Fe_2O_3, pH 7·5, and layer silicate clay largely montmorillonite.
5. Scott clay B, 7–28 in., a poorly drained soil developed from a calcareous material from Kimball county, Nebraska, with 0·75 per cent. extractable Fe_2O_3, pH 6·7, and layer silicate clay largely montmorillonite.
6. Dewey silt loam, A_2 horizon, 2–12 in., a limestone-derived Reddish Podzolic soil from Eastern Tennessee, with 3·3 per cent. extractable Fe_2O_3, pH 5·5, and kaolinic layer silicate clay.
7. Rosebud clay loam, B_2 horizon, 10–18 in., a Dark Brown (Chestnut) soil from Kimball County, Nebraska, with 0·82 per cent. extractable Fe_2O_3, pH 7·1, and layer silicate clay mainly illite and montmorillonite.
8. Barnes silt loam, A horizon, 3–12 in., a Chernozem from North Dakota, with 0·77 per cent. extractable Fe_2O_3, pH 7·5, and layer silicate clay largely montmorillonite.
9. Barnes silt loam, 28–54 in., from the same profile as 8, with 0·55 per cent. extractable Fe_2O_3, and pH 8·0.
10. Barnes silt loam, 54–64 in., from the same profile as 8, with 0·93 per cent. extractable Fe_2O_3, and pH 8·0.

The second set of samples includes the three layers 0–6 in., 18–24 in., and 36–42 in. of two Miami silt loam profiles, one from Kirwin farm and the other from Mitchell farm of Dane County, Wisconsin. The Kirwin farm soil was developed on calcareous parent material and the Mitchell farm soil on acid parent material. Both soils have been cultivated and the surface 6-in. layers have been limed to pH 7. The available P test is low in the surface soil, yet the corn and oats crops respond little to phosphate fertilizer in field experiments.

The third set of samples includes six treatments in four replications from fertilizer experimental plots on Almena silt loam near Owen, Clark County, Wisconsin, representing three levels of lime, 0, 4·5, and 8 tons per acre, respectively, and two levels of phosphate, check and high rate of monocalcium (super-) phosphate. The plots were laid down in 1944. A 4-year rotation of corn, oats, hay, and hay was followed. Lime was applied at the beginning of the experiment and phosphate fertilizer was applied to the high-phosphate plots on corn and oats of

each rotation. Potash fertilizer was applied as needed in the different productivity levels developed. Nitrogen was derived from legume and manure application. Soil samples were collected in October of 1954 and September of 1956.

Soil-Phosphorus Fractions in Soils Representing some Major Soil Groups

The inorganic phosphorus fractions (Table 1) of various soil genetic groups show three different patterns of distribution. First, in the highly

TABLE 1

Soil Inorganic Phosphorus Fractions of Samples Representing some Major Soil Groups, p.p.m. of P

Soil, horizon, and depth (in.)	*Soil group*	*Soil* pH*	*Extractable* Fe_2O_3(%)	*Ca-phos.*	*Al-phos.*	*Fe-phos.*	*Reductant soluble Fe-phos.*	*Occluded Al-phos.*
Wahiawa A, 10–18	Latosol	6·7	10·1	10	20	123	504	97
Catalina A, 12–36	Latosol	6·2	18·2	6	0	42	320	40
Miami A_3, 12–16	G-B. Pod.	5·8	1·4	45	48	100	73	6
Miami C_1, 46–58	G-B. Pod.	7·8	1·2	525	21	10	7	Trace
Scott B, 7–28	Ground water	6·7	0·75	162	85	48	16	12
Dewey A_3, 2–12	Red. Pod.	5·5	3·3	32	2	22	26	19
Rosebud B_2, 10–18	D. Brown	7·1	0·82	122	11	8	9	6
Barnes, 3–12	Chern.	7·5	0·77	155	18	8	Trace	Trace
Barnes, 28–54	Chern.	8·0	0·55	190	11	11	Trace	Trace
Barnes, 54–64	Chern.	8·0	0·93	185	6	3	Trace	Trace

* At moisture saturation.

weathered Catalina Latosol and Wahiawa Latosol, only a very small amount of phosphorus is present as calcium phosphate and aluminium phosphate. Most of the phosphorus is present in the form of iron phosphate, the majority of which is occluded. These two soils, although low in aluminium phosphate, contain considerable occluded aluminium phosphate.

Second, the three Chernozem samples of Barnes silt clay loam are dominant in calcium phosphate with little iron and aluminium phosphate and no occluded phosphate at all. Rosebud clay loam (B_2 horizon) developed from calcareous material and the C_1 horizon of Miami silt loam with a pH of 7·8 are also dominant in calcium phosphate, and are relatively low in both aluminium and iron phosphates.

Third, Miami silt loam A_3 horizon (pH 5·8) and Scott B horizon (pH 6·7), both developed from calcareous parent material, occupy an intermediate position. The phosphorus is fairly evenly distributed among the three forms of phosphate. Dewey silt loam (pH 5·5), also developed from limestone material, has most of its inorganic phosphorus in calcium phosphate and iron phosphate, but very little in aluminium phosphate. The total amount of phosphorus of this soil is, however, very low.

Determination of the inorganic forms of soil phosphorus provides a means of quantitative measurement of soil chemical weathering.

Extremes of weathering are shown graphically (Fig. 1) by exponential functions to left (little weathered) and right (much weathered), while intermediate stages are represented by sigmoidal curves representing combinations of the two extremes. Sensitive changes occur as a function of soil depth and other chemical weathering factors (discussed under

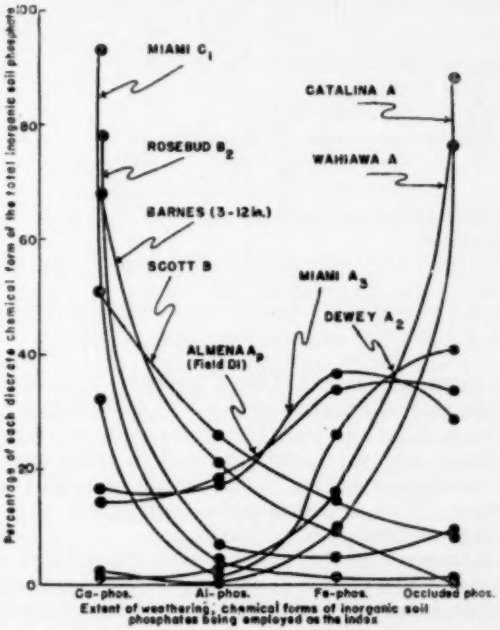

FIG. 1. The percentage of the discrete chemical forms of inorganic soil phosphates plotted as a chemical weathering sequence.

'conclusions'). These changes are more sensitive than shown by the mineral colloid weathering sequence of Jackson *et al.* (1948, 1952). The proposed functionality extends the relationship noted by Bauwin and Tyner (1954) between reductant soluble phosphorus and chemical weathering of soils.

The Distribution of Soil Phosphorus in Two Miami Profiles

It was found in previous studies (Marriott, 1955) that crop response to added phosphate fertilizer did not correlate well with soil phosphorus tests in the surface plough layer of Miami silt loam in several locations. The distribution of the various discrete chemical forms of phosphate in the successive layers was determined (Chang and Jackson, 1957*a*) for two of the locations.

The soil pH values, 0·002 N H_2SO_4 extractable phosphorus (Truog,

1930) and extractable iron oxides (Aguilera and Jackson, 1953) were also determined for reference (Table 2).

TABLE 2

Fractions of Soil Phosphorus in Two Miami Profiles, p.p.m. of P

Soil:	*Miami* (*Kirwin farm*)			*Miami* (*Mitchell farm*)		
Depth (in.):	0–6	18–24	36–42	0–6	18–24	36–42
Soil pH*	7·0	5·3	6·1	7·1	5·3	4·9
0·002 N H_2SO_4 P	18	28	64	15	28	72
Extractable Fe_2O_3, %	0·8	1·5	1·1	0·8	1·6	1·7
Ca-phosphate	59	80	158	49	50	113
Al-phosphate	16	18	6	20	59	64
Fe-phosphate	78	157	75	49	157	141
Reductant soluble Fe-phosphate	138	217	121	148	178	158
Occluded Al-phosphate	8	10	10	..	..	..
Organic P	52	..	3	70	6	0
Added total P	351	482	373	336	450	476

* At moisture saturation.

The two profiles differ in pH of the C horizon. That of Kirwin profile is less acid than that of Mitchell profile. The pH values of the surface and second layers of both soils are almost the same, neutral in the surface soil due to liming and very acid (pH 5·3) in the second layer. The extractable iron oxide is higher in the second and third layers than in the surface layer. The accumulation of extractable iron oxide in the second layer is an indication of podzolization.

The relative amounts of the four inorganic phosphates in the various layers of the two profiles (Table 2), in increasing order of abundance, are aluminium phosphate, calcium phosphate, iron phosphate, and reductant soluble iron phosphate, the third layer of Kirwin profile being an exception in that the amount of calcium phosphate is higher than both iron phosphate and reductant soluble iron phosphate. All these four forms of inorganic phosphates are, in general, higher in the subsoil than in the surface soil.

The aluminium-phosphate content in the Kirwin profile is the same in the surface and second layer, but decreases in the third layer in which both the pH and calcium phosphate are higher. In the Mitchell profile the aluminium-phosphate content exceeds calcium phosphate in the second layer and increases more in the acid third layer, although calcium phosphate also increases.

The distribution of iron phosphate in the three layers of the two profiles has the same tendency as that of aluminium phosphate, although the amount is much higher than that of aluminium phosphate. Reductant soluble iron phosphate accounts for about 30–50 per cent. of the total inorganic phosphorus. The highest content is in the second layer where the extractable iron oxide is also the highest.

The lack of crop response to the added phosphate fertilizer on these

soils in which the phosphorus test of the surface 6 in. is low is attributed to two factors. First is the higher available phosphorus in the subsoil down to 3½ ft. (Table 2). Second is the release to the crop of phosphorus from aluminium and iron phosphate from the surface soil by the lowered Al and Fe activity resulting from increase of pH through liming (Cole and Jackson, 1951). The 0·002 N H_2SO_4-extracted phosphorus in the various layers is correlated mainly with the calcium phosphate, also somewhat with aluminium and iron phosphate, but not with the reductant soluble iron phosphate. The former three forms of phosphates are all available to plant use, if their specific surface area is sufficiently large (Kittrick and Jackson, 1956; Olsen and Watanabe, 1957). The latter form probably is not available for plant use, except through an unusual degree of poor drainage (paddy soils) under which iron-oxide reduction is effected. Little release evidently can be expected under the local anaerobic condition around decaying organic-matter particles.

The Fate of Fertilizer Phosphate added to Almena Silt Loam

For the purpose of determining how liming and cropping influence the distribution of applied phosphate fertilizer among the various forms, or the fate of applied phosphate fertilizer, soil-phosphorus fractionation was carried out on some samples from fertility experimental plots (Table 3). The three levels of lime cover pH levels of 4·7 to 6·7. The 0·002 N H_2SO_4-extractable-phosphorus level in the plots with high rate of phosphate fertilization is about three times that of the check plots. Liming significantly increases the available phosphorus test of the high-phosphate plots, but not of the unphosphated plots.

The inorganic phosphorus in Almena silt loam, a podzolic soil with very low pH (below 5), exists in large part as iron phosphate and reductant soluble iron phosphate. Calcium phosphate is next in abundance and aluminium phosphate is the least. Application of lime has little effect on the relative abundance of these discrete forms of the native phosphorus in the unfertilized soil. On the other hand, application of soluble phosphate fertilizer greatly increases the amount of aluminium and iron phosphate at all three lime levels (Fig. 2), but increases the calcium phosphate only slightly at the highest lime level. Reductant soluble iron phosphate is not affected by liming or fertilization. The relatively small increase of calcium phosphate through phosphate-fertilizer application regardless of lime level is probably attributable to both crop removal and the precipitation of applied phosphate as the less soluble iron and aluminium phosphates. However, liming did definitely keep more applied phosphate as calcium phosphate, which is more available to plants than other forms of phosphates. The formation of reductant soluble iron phosphate must be through a slow process related to soil genesis, and not much affected by the recent fertilizer application, in accord with corresponding data of Dean (1938) on Rothamsted soils.

Conclusions

The formation of the various discrete chemical forms of phosphate in the soil is apparently related to soil factors such as pH, activities of various

TABLE 3

Phosphorus Fractions in Cultivated Almena Silt Loam, 1956, p.p.m. of P

Lime level	*Field*	*Soil* pH*	0·002 N H_2SO_4 *extractable* P, *p.p.m.*	Ca-*phos.*	Al-*phos.*	Fe-*phos.*	*Reductant soluble* P*	*Organic* P*
			Check—No phosphorus added					
No lime	A1	..	10	64	22	85	..	..
	B1	..	20	48	20	70	..	..
	C1	..	16	45	22	73	..	..
	D1	4·9	14	33*	41*	78*	78	129
	Average	..	15	48	26	77	..	..
Lime, 4·5 tons per acre	A21	..	13	65	18	85	..	..
	B21	..	15	61	26	81	..	..
	C21	..	17	70	19	69	..	..
	D21	6·2	14	38*	28*	80*	82	182
	Average	..	15	59	23	79	..	..
Lime, 8 tons per acre	A41	..	17	58	19	61	..	..
	B41	..	17	58	19	65	—	..
	C41	..	15	45	22	55	..	..
	D41	6·7	19	33*	25*	68*	77	172
	Average	..	17	49	21	62	..	..
			High phosphorus fertility level†					
No lime	A5	..	62	51	79	145	..	..
	B5	..	49	42	89	137	..	..
	C5	..	78	61	115	142	..	..
	D5	4·7	59	40	108	152	53	172
	Average	..	62	49	98	144	..	..
Lime, 4·5 tons per acre	A25	..	70	66	72	145	..	..
	B25	..	67	57	138	152	..	..
	C25	..	80	72	100	165	..	..
	D25	5·9	80	52	84	137	72	141
	Average	..	74	62	99	150	..	..
Lime, 8 tons per acre	A45	..	74	77	88	137	..	..
	B45	..	74	76	92	150	..	..
	C45	..	83	78	83	156	..	..
	D45	6·6	92	73	100	145	70	203
	Average	..	81	76	90	147	..	..

* Determinations made on samples collected from field D in October 1954. The pH values were determined at moisture saturation.

† Conventional row fertilizer following 280 lb. of P per acre initial application as superphosphate 12 cropping years previously.

cations, solubility products of the various phosphates, degree of chemical weathering, and fertilizer practice. At the initial stage of weathering and also right after the application of phosphate fertilizer, calcium phosphate and aluminium phosphates are more likely to be formed than iron phosphate. This is attributed to the relatively higher activities in the soil of calcium and aluminium ions than iron ions, which are controlled by the activities of the respective cations of calcium carbonate, aluminosilicates and gibbsite, and iron oxides. Aluminium phosphate at first increases more than iron phosphate (Table 1). As time elapses, the

calcium and aluminium phosphates change gradually into iron phosphate which is the least soluble among them (Chang and Jackson, 1957*b*). Iron activity associated with iron oxide increases with decrease in pH

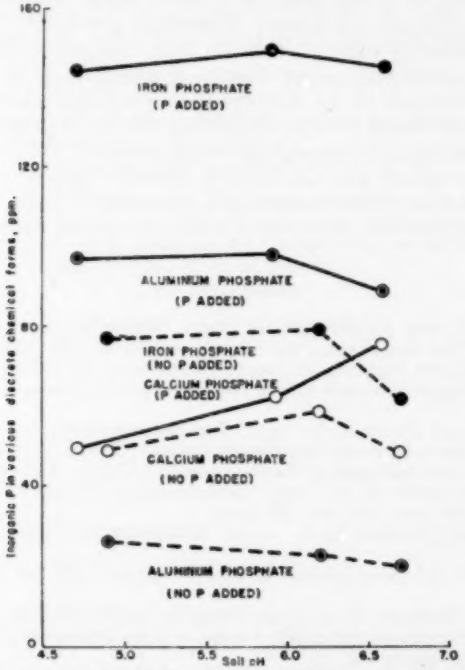

FIG. 2. The distribution of the added phosphate into the various discrete chemical forms in Almena silt loam variously limed.

(Kittrick and Jackson, 1955*a*) and with increasing amount of iron oxides in soil (Olson, 1947). The inference drawn from the Latosol analyses (Table 1) is that iron phosphate and also a portion of aluminium phosphate and aluminium-iron phosphate (barrandite-like) finally become occluded by an iron-oxide coating, formed in the course of chemical weathering.

Since the soil is a heterogeneous particulate system, the change from one phosphate form to the other requires a long time. The occluded phosphate is the most weathering-resistant form and accumulates during several centuries of time. Thus the formation and transformation of the various phosphate species according to the chemical principle of solubility product, following the order of calcium, aluminium, iron, and occluded phosphate, corresponds to increasing stages in a weathering sequence (Fig. 1), due to their different stabilities.

Phosphate fertilizer added to the soil is changed into all the three forms of phosphate (Table 3), calcium, aluminium, and iron phosphates,

not only in acid soils but also at neutral reactions according to the principle of solubility product (Kittrick and Jackson, 1955*b*, 1955*c*, 1956; Chang and Jackson, 1957*b*). Since calcium is more soluble than the other forms of phosphates, it is more easily removed by crops or shifted to the less soluble forms. Therefore, a neutral reaction of a soil does not necessarily indicate that the soil contains a larger portion of calcium phosphate than other forms of phosphates, as shown by the phosphorus fractions of the Almena silt loam (Table 3) and the surface soils of the two Miami profiles (Table 2). However, increase of calcium activity and raising of pH value by liming definitely favour the formation of calcium phosphate and the release, through repression of Al and Fe activity (Cole and Jackson, 1951), of phosphorus from the aluminium and iron phosphate for plant use during a cropping season.

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ISOTOPICALLY EXCHANGEABLE PHOSPHORUS IN SOILS

III. THE FRACTIONATION OF SOIL PHOSPHORUS

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Summary

Phosphate residues in the soil were subdivided into three fractions on the basis of isotopic exchange of orthophosphate ions between the soil and the soil solution. It was observed that the total labile phosphorus was a smaller fraction of the total phosphorus in the heavier soils (*c.* 20 per cent. clay) than in the lighter soils (1–10 per cent. clay). This could be partly attributed to a higher organic-phosphorus content in the heavier soils. In comparable soils, recent manuring with superphosphate increased the ratio of the rapidly labile phosphate to the total labile phosphate; in the soils of lower clay content, this ratio was higher than the corresponding ratios in the heavier soils. The recovery of phosphorus added at a moderately heavy rate was estimated by this method of fractionation in soils incubated for periods up to 3 months after treatment. Recovery of added phosphorus in the total labile fraction was incomplete for the calcareous soils, as compared to a 100 per cent. recovery in a neutral soil of similar clay content. Moreover, a redistribution of phosphorus with time was observed in the calcareous soils *within* the total labile fraction, no such effect being observed with the neutral soil. This was attributed to the presence of internal surfaces on the calcium carbonate present.

Introduction

In chemical methods used to assess the value of phosphate residues in the soil, three factors have been studied—nature of extractant, its concentration, and time of contact with the soil. The aim of these methods is to determine the relative 'availability' of different fractions of the total soil phosphorus. Thus the relative availability of phosphate residues in the soil has been assessed by the use of (*a*) the same extractant at different concentrations (Fisher and Thomas, 1935; Hibbard, 1931), (*b*) the same extractant at different pH values (Holman, 1936; Stelly and Pierre, 1943). In these determinations the phosphorus content of the extractant solution is measured at equilibrium.

Other measurements of relative solubility are of a dynamic character in which the same extractant is in contact with the soil for various times; an estimate of the relative 'availability' of the soil phosphorus is made in terms of the phosphorus extracted at two different times (Fisher and Thomas, 1935). Fractionation on a time basis is thus achieved.

Extraction methods, although arbitrary, serve as a practical guide to 'availability'. From the literature it is obvious that there are various conceptions of the ability of plant roots to obtain nutrient ions from the soil. The factors which contribute to a theoretically sound basis for such evaluation are discussed elsewhere (Talibudeen, 1957).

Isotopic exchange with ^{32}P and 'relative availability'. Several workers have reported the isotopic exchange of orthophosphate ions between the solution and the solid in soil suspensions, using ^{32}P as tracer. Despite the variety of conditions used in such experiments, wherever the fractional isotopic exchange is reported in relation to the time factor the total isotopically exchangeable phosphate has been found to be made up, broadly speaking, of rapidly and slowly exchanging fractions (Barbier *et al.*, 1954, 1955; McAuliffe *et al.*, 1948; Seatz, 1954; Wiklander, 1950). The isotopically exchanging fraction is considered to be the 'surface phosphorus' in the soil and is in general correlated with the amounts of soil phosphorus utilized by plants to the same degree as tagged phosphate applied uniformly to the soil in pots (Barbier *et al.*, 1955; Gunnarsson and Fredriksson, 1953; Olsen, 1953).

In work reported earlier (Talibudeen, 1957; Wiklander, 1950), the phosphate equilibria in a moist soil were discussed, together with the effect of various factors on these equilibria measured by an isotopic exchange method (Talibudeen, 1954). The distribution of rapidly and slowly exchanging phosphate fractions in a soil was defined. Examination of several isotopic-exchange curves obtained by the above method on soils from Rothamsted and Woburn suggests that the process of rapid exchange is always completed under these conditions after 24 hours of exchange. The results of the examination of several soils of known manurial history by the isotopic-exchange method are reported in this paper, based on a time fractionation of their phosphate residues.

There appears to be no evidence in the literature on the short-term effect of inorganic phosphate added to soils as assessed by isotopic-exchange methods. Many extraction methods can give a clear indication of phosphate requirements (Warren, 1956), but it is unlikely that they would give a quantitative picture of the distribution of added phosphate.

Materials

Table 1 gives data on the soils used. For the experiment on the short-term effect of added orthophosphate, the Exhaustion Land soils and the Highfield soil were sprayed with a solution of monocalcium phosphate so as to add 10 mg. P per 100 g. soil and give a moisture content at about field capacity. All samples were ground to pass a 60-mesh sieve and were continuously mixed during the spraying. The phosphate-treated and untreated samples were stored in closed containers at $25 \pm 1°$ C., sub-sampled at 1-, 2-, and 3-month intervals and air-dried.

Methods

Two procedures were employed for these experiments in which 0·5 g. soil was shaken for over 20 hours at a controlled temperature (25 or 30° C.) in 100 ml. 0·001 M ammonium-citrate buffer in 0·02 M KCl whose pH was adjusted to the pH of the soil in 0·01 M $CaCl_2$ (Talibudeen, 1954). The suspensions were then tagged with a known amount of 'carrier-free' ^{32}P, the flasks agitated and sampled after known periods.

TABLE I

Description of Soils

Serial no.	*Soil description*	*Phosphate applied*	$CaCO_3$ (%)	pH *in* 0·01 M $CaCl_2$	*Mechanical analysis*•				*Total phosphorus* P_t (*mg./100 g.*)
					Clay (%)	*Silt* (%)	*Fine sand* (%)	*Coarse sand* (%)	
Rothamsted Soils									
1	Exhaustion Land	(*a*) None	1	7·5	18·7	28·0	46·3	5·5	42·6
2		(*b*) F.Y.M. before 1901	1	7·5	19·0	28·5	44·7	4·2	65·1
3		(*c*) Superphosphate before 1901	1	7·5	19·3	29·3	44·6	4·4	67·8
4	Highfield	..	< 0·1	6·7	20·3	24·3	44·1	5·3	90·6
5	Sawyers	..	Nil	5·2	22·7	22·0	42·0	10·3	56·4
6	Broadbalk	(*a*) No phosphate or ammonium sulphate	2·9	7·4	..	..	..	..	60·5
7		(*b*) Only ammonium sulphate	0·7	6·9	19·3	26·0	47·2	5·1	64·5
8		(*c*) Superphosphate	0·7	6·9	..	..	..	..	115·2
9	Four-course rotation	(*a*) One year after superphosphate	1	7·4	..	..	..	..	60·6
10		(*b*) Two years after superphosphate	1	7·5	..	..	..	..	62·0
11		(*c*) Five years after superphosphate	1	6·9	23·0	23·5	42·9	8·4	65·2
12	Four-course rotation	(*a*) One year after Gafsa Rock phosphate	1	7·4	..	..	..	..	62·8
13		(*b*) Five years after Gafsa Rock phosphate	1	7·4	..	..	..	..	64·9
Soils from the Forestry Commission Nurseries									
14	Kennington (long-term)	(*a*) No phosphate	Nil	5·3	11·5	5·7	18·1	61·0	47·2
15		(*b*) Superphosphate	,,						51·1
16	Old Kennington	(*a*) No phosphate	,,	6·0	10·5	6·7	19·6	60·5	51·7
17		(*b*) Superphosphate	,,	1·0	..	..	..	..	62·5
18	Wareham (long-term)	(*a*) No phosphate	,,	5·4	..	..	..	..	5·8
19		(*b*) Superphosphate	,,	5·4	..	..	..	..	7·3
20	Wareham	(*a*) No phosphate	,,	4·7	..	..	..	..	6·6
21		(*b*) Superphosphate	,,	4·9	1·0	5·3	38·3	53·0	11·5
22		(*c*) Gafsa Rock phosphate	,,	5·2	..	..	..	..	13·9
23		(*d*) Basic slag	,,	5·4	..	..	..	..	11·6
24	Ringwood	(*a*) No phosphate	,,	4·5	3·0	5·5	40·3	49·6	25·7
25		(*b*) Superphosphate	,,	4·9					33·4

• Mr. W. C. Game of the Physics Department was responsible for these analyses. (In each group, the analysis of one representative soil is given.)

The isotopically exchangeable phosphorus P_e at any time could be calculated from the fraction of radioactivity (f_t) left in solution by the expression:

$$P_e = \frac{P_s}{f_t},$$

where P_s is the phosphorus determined in solution.

The solution was extracted from the suspension by centrifuging at 15,000 r.p.m. for 5 minutes. A temperature rise of up to 5° C. was observed during centrifuging, but the effects of this were minimized by centrifuging only the cloudy suspension left after standing the whole suspension for about 2 hours.

The standard deviation in the value of P_e was $\pm 2{\cdot}5$ per cent.

Procedure A. 3–5 μC of ^{32}P were added, the flasks shaken continuously at 60 oscillations per minute, and 0·5-ml. samplings were taken at various time intervals from $\frac{1}{2}$ to 200 hours. The 0·5-ml. volumes were dried on aluminium planchettes under an infra-red lamp and counted in a methane-flow proportional counter. The fractional activity left in solution at any time was read off the smoothed curve of the decrease in radioactivity in solution with time.

Procedure B. Under 1 μC of ^{32}P was added, the flasks were shaken by hand for 1 minute six times a day; two flasks per soil were filtered 24 hours after sampling and two flasks at 150 hours. The radioactivity was estimated in an M6 Geiger counter.

In each procedure, the amount of ^{32}P added was estimated by adding the same amount of ^{32}P to three flasks containing 100 ml. of the citrate-KCl buffer and 5, 10, and 15 γ of P as orthophosphate. The β-counts in these could be reproduced by proportional counting in solid samples or by Geiger counting in liquid samples to within the statistical error of counting.

The total phosphorus in the soil was determined by digesting 2 g. soil in 60 per cent. $HClO_4$.

Estimation of Phosphorus. (1) Citrate extracts: A modification of the Truog and Meyer (1929) method was used; the phosphomolybdate complex was produced by adding 4 ml. of the acid ammonium-molybdate solution containing from 1 to 100 γ P. 0·4 ml. of the freshly prepared stannous-chloride solution was then added and the molybdenum-blue colour developed was estimated after 10 minutes. The standard curve was obtained with P standards containing 0·001 M ammonium citrate. (2) Perchloric-acid extracts for total-P determinations: the method of Hanson (1950) was used.

Results

Long-term effect. In Tables 2, 3, and 4 the isotopically exchangeable phosphorus values at 24 hours (P_{24}) and 150 hours (P_{150}) are given as fractions of P_{150} and the total phosphorus P_t, respectively. In the first three columns of these tables, the P_{24}, P_{150}, and P_t values are also given. These subdivide the soil phosphorus into rapidly, slowly and very

TABLE 2

Labile P *in Some Rothamsted Soils*

Serial no.	*Soil description*	*mg.* P/100 *g.*				
		P_{24}	P_{150}	P_t	P_{24}/P_{150}	P_{150}/P_t
1	Exhaustion Land: Nil	2·9	4·8	42·6	0·61	0·11
2	F.Y.M.	7·7	11·0	65·1	0·70	0·17
3	Superphosphate	6·7	9·2	67·8	0·73	0·14
4	Highfield	13·6	16·0	90·6	0·85	0·18
5	Sawyers	5·0	9·0	56·4	0·56	0·16
6	Broadbalk: Nil	2·6	4·5	60·5	0·58	0·08
7	$(NH_4)_2SO_4$ only	2·7	7·6	64·5	0·36	0·12
8	Superphosphate	18·7	24·1	115·2	0·78	0·21

TABLE 3

Labile P *in Rothamsted 4-course Rotation Experiments*

Serial no.	*Soil description*	*mg.* P/100 *g.*				
		P_{24}	P_{150}	P_t	P_{24}/P_{150}	P_{150}/P_t
	4-course rotation:					
9	1st year after superphosphate	7·7	8·4	60·6	0·92	0·14
10	2nd year after superphosphate	5·9	7·8	62·0	0·76	0·14
11	5th year after superphosphate	3·9	8·0	65·2	0·49	0·12
12	1st year after Gafsa rock phosphate	3·4	5·5	62·8	0·62	0·09
13	5th year after Gafsa rock phosphate	3·4	5·5	64·9	0·62	0·09

TABLE 4

Labile P *in Acid Soils of Medium and Light Texture*

Serial no.	*Soil description*	*mg.* P/100 *g.*				
		P_{24}	P_{150}	P_t	P_{24}/P_{150}	P_{150}/P_t
14	Kennington long-term: Nil	8·1	12·4	42·2	0·65	0·26
15	Superphosphate	14·1	15·5	51·1	0·91	0·30
16	Old Kennington: Nil	9·5	11·5	51·7	0·83	0·22
17	Superphosphate	21·6	22·5	62·5	0·96	0·36
18	Wareham long-term: Nil	1·16	1·45	8·45	0·80	0·17
19	Superphosphate	1·83	2·35	8·75	0·78	0·27
20	Wareham: Nil	0·88	1·3	6·6	0·68	0·20
21	Superphosphate	3·8	4·0	11·5	1·00	0·35
22	Gafsa rock phosphate	3·4	3·4	13·9	1·00	0·24
23	Basic slag	3·6	3·6	11·6	1·00	0·31
24	Ringwood: Nil	8·0	8·7	25·7	0·92	0·34
25	Superphosphate	14·7	14·7	33·4	1·00	0·44

slowly exchangeable fractions given by P_{24}, $P_{150}-P_{24}$ and P_t-P_{150}, respectively.

TABLE 5

The Recovery of 10 mg. P per 100 g. Soil added as Monocalcium Phosphate to four Rothamsted Soils Incubated at 25° C. and Field Capacity

(The figures in the table are the difference in mg. P per 100 g. soil in labile P estimated by isotopic exchange in treated and control samples.)

Treated soil sampled after incubation for:	Exhaustion land soils							
	Nil		F.Y.M.		Superphosphate		Highfield	
	Amount of P in mg. recovered after isotopic exchange for:							
	24 hrs.	150 hrs.	24 hrs.	150 hrs.	24 hrs.	150 hrs.	24 hrs.	150 hrs.
1 month	6·3	6·8	7·0	7·3	7·3	7·6	7·5	9·9
2 months	4·9	6·6	5·7	7·1	5·8	7·1	..	..
3 months	4·4	6·5	5·2	7·0	5·4	7·9*	7·5	10·1
Change in P_{24} between 1 and 3 months	1·9		1·8		1·9		0	

* See text.

Short-term effect. The recovery of monocalcium phosphate added to four soils at the rate of 10 mg. P per 100 g. soil after 24 and 150 hours of isotopic exchange is given in Table 5. This recovery is the difference in P_{24} and P_{150} values for treated and untreated soils. Fig. 1 graphically expresses the redistribution of isotopically exchangeable phosphorus by the variation of the ratio P_{24}/P_{150} during the 3-month period.

Discussion

The change in the character of phosphate residues is affected by various factors. Firstly, the removal of PO_4 from readily exchangeable sites, secondly, the physical or chemical transformation of PO_4 into less accessible or less labile forms, and thirdly, the formation of slightly soluble compounds during the drying and wetting cycles.

Long-term effects

P_{150}/P_t *ratio.* In general, the total 'isotopically exchangeable' or labile phosphorus as a fraction of the total phosphorus (P_{150}/P_t) appears to be a function of silt+clay content primarily. The presence of non-labile organic-phosphate residues may also contribute to the change in this ratio between the two soil groups. Loss-of-ignition data suggest that the average level of organic *matter* may be higher in Rothamsted soils than in the Nursery soils, but in the absence of reliable data on the organic *phosphorus* content of these soils it is not possible to discuss this in detail. In all Rothamsted soils examined so far, acid, neutral, or calcareous, this ratio never exceeds 0·18, the range being from 0·04 to 0·18. In the medium and light acid soils from the Forestry Commission Nurseries, this ratio varies between 0·20 and 0·35.

The variation observed within each range is due to residues of phosphate applications. The 'no-phosphate' plots in Exhaustion Land and

Broadbalk give an average ratio of 0·10, this being more than doubled in the lighter soils from the Forestry Commission Nurseries. On the heavier soils of higher average P content, phosphate application causes a small but significant increase in this ratio; the medium textured soils from Kennington of comparable phosphorus content show a similar increase. On the lighter soils of low P content, the P_{150}/P_t ratio is quite sensitive to phosphate applications.

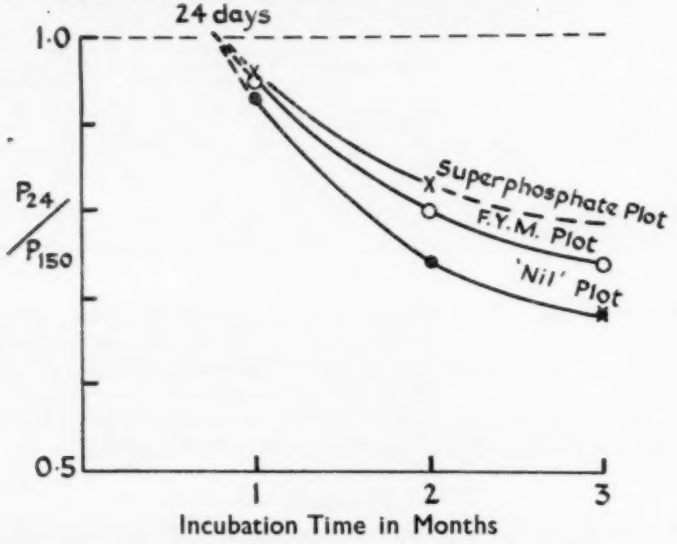

FIG. 1. The recovery of P added as monocalcium phosphate to three Exhaustion Land soils incubated at 25° C. and at field capacity. The ordinate is the ratio of the differences in the isotopically exchangeable phosphorus between 'P-treated' and 'control' samples after 24 and 150 hours of isotopic exchange.

P_{24}/P_{150} *ratio.* The more interesting comparison is between the rapidly exchangeable and total labile phosphorus.

In the Exhaustion Land, residues of F.Y.M. and superphosphate after 50 years are clearly reflected in a ratio of 0·73 over 0·61 for the untreated plot (Table 2). A marked depression in the ratio is observed in the Broadbalk 'no-phosphate' plots where only ammonium sulphate was applied. This may be due to an increased preferential utilization of the readily available phosphorus by the crop over the 'nil' plot, or the mobilization of the very slowly available fraction by the addition of $(NH_4)_2SO_4$. The latter explanation appears to be favoured by the fact that the P_{24} values for both soils are identical, whilst the 'slowly' exchangeable fraction is increased at the expense of the 'very slowly' exchangeable part.

Table 3 gives results up to 5 years after application for 4-course rotation experiments on a calcareous Rothamsted soil in which superphosphate and Gafsa rock phosphate were applied initially. The P_{150}

values show little change accompanied by a marked fall in the P_{24} values, a considerable part of which must be due to removal of P by cropping. When Gafsa is applied little change is observed in either values, the total labile P being of the same order as the untreated plots in Hoosfield and Broadbalk.

With soils of lighter texture, a progressive increase in both ratios is observed; the difference in the P_{24}/P_{150} ratio with untreated and treated soils is maintained with one exception (Wareham long-term, Table 4). Generally, the lower the total P in the untreated soil the greater is the increase observed in the P_{150}/P_t ratio; the higher P_{150}/P_t ratios suggest that these soils could be more rapidly exhausted by intensive cropping. In the light acid soils, all the labile P is readily exchangeable, although it is noticeable that when Gafsa is applied (Wareham, Table 4) the P_{150}/P_t ratio is not very different from the untreated soil.

Since the silt+clay content appears to be of some importance in deciding the nature of the P residue, it is interesting to compare the distribution of P in soils of roughly the same pH from 'light', 'medium', and 'heavy' areas. Thus the untreated Old Kennington Soil (Table 4) has a slightly larger fraction of its total P as labile P than Rothamsted Highfield soil (Table 2), although its total P content is nearly half that of the Highfield soil. In addition, the P_{24}/P_{150} ratios in both soils are practically identical. The untreated Kennington (long-term) soil (Table 4) which compares favourably in pH and total P with Sawyers (Table 2) has both ratios very much higher than the latter soil has.

The Ringwood and Wareham soils, highly acid and of light texture, have shown a tendency to retain recently added phosphate in the readily labile fraction (Table 4), and the total labile P constitutes a very high percentage of the total soil phosphorus.

Short-term effect

Of the four soils tested here, the Exhaustion Land soils contain small amounts (average 1 per cent.) of $CaCO_3$; the Highfield soil contains practically no $CaCO_3$. From Table 5 it is clear that one month after the P treatment only two-thirds of the applied P is recovered in the total labile P in the untreated Exhaustion Land soil, whereas recoveries of 71 per cent. and 75 per cent. are obtained for the F.Y.M.- and superphosphate-treated soils respectively. Furthermore, a very slow decrease in total labile P is observed for all Exhaustion Land soils. The asterisked figure (Table 5) of the recovery for the superphosphate plot after 150 hours' exchange appears to be high; a more likely figure is 7·0 mg. obtained from the P_{24} value (Table 5) and the extrapolated value of 0·785 for the P_{24}/P_{150} ratio (Fig. 1). Thus the unmanured soil relegates one-third and the manured soils about one-quarter of the added P to the *very-slowly* labile fraction in a 1–3-month period. A more significant fact is that in these three calcareous soils there is a decrease of one-fifth of the added phosphorus in the rapidly labile P to the benefit of the *slowly* labile P. Thirdly, in a similar experiment with a non-calcareous soil of high P status from the same locality, *all* the P added is recovered in the total labile P, of which three-quarters is *rapidly* labile P.

It would thus appear that the decreased recovery of added P in the labile fraction follows the increased exhaustion of the soil in the order untreated soil > F.Y.M.-treated > superphosphate-treated > Highfield. This decreased recovery is equivalent to the adsorption of added PO_4 ions on sites with a high energy of adsorption; consequently, these PO_4 groups exchange isotopically with PO_4 ions in solution only very slowly. This adsorption process is almost complete in less than a month; experiments with shorter periods of incubation would be necessary to be more precise than this.

In addition the Exhaustion Land soils show a redistribution of 1·9 mg. P of added PO_4 per 100 g. of soil from the readily to the slowly available part of the labile phosphate. The constancy of this figure, despite the difference in the state of exhaustion of the untreated soil on the one hand and of the F.Y.M. and superphosphate plots on the other, suggests that this redistribution may be due to a shift of the adsorbed PO_4 to less accessible sites on the calcium carbonate fraction in these soils. It is clear from Fig. 1 that after 3 months of incubation this process is not yet at an end. It is also equally clear from the extrapolation of the P_{24}/P_{150} ratio for the recovered phosphate to unity that all the added phosphate (after subtracting the part removed by unsaturated adsorption sites in the soil created by the exhaustion process) is in the readily-labile fraction up to 24 days after the phosphate treatment. A full picture of the phenomenon can only be obtained by similar measurements on an extended time scale (*a*) on soils of similar phosphate status but widely varying calcium carbonate contents, and (*b*) on standard samples of calcium carbonate.

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THE ALKALINE NITROBENZENE OXIDATION OF SOIL ORGANIC MATTER

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Summary

The yields of syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde obtained by alkaline-nitrobenzene oxidation of soil organic matter indicate the extent to which lignin-derived material is present. A number of soils, peats, and peat fractions have been oxidized by this method and the phenolic aldehydes formed have been separated and determined by a micro-technique. The results indicate the presence in soil organic matter of significant amounts of syringyl, guaiacyl, and *p*-hydroxyphenyl residues which are almost certainly derived from lignin. The yields of aldehydes from mineral soils accounted for about 0·5–1·0 per cent. of the total organic carbon; from peats for about 1·0–4·0 per cent. There was evidence of a correspondence between the relative amounts of the three aldehydes obtained from the soil organic matter and from the parent plant material. The results for a peat profile indicated a tendency for the yield of aldehydes to increase with depth of the horizon; the reverse was found with a pine-forest soil profile. Peat fractions all gave some aldehydes on oxidation, but there were marked differences in the levels; the highest yield, almost 7 per cent., was obtained from a humic-acid fraction soluble in ethanol-benzene. Hydrolysis of the humic-acid fractions with dilute hydrochloric acid markedly depressed the yields of aldehydes obtainable on oxidation.

THE present state of knowledge concerning the chemical nature of soil organic matter has recently been reviewed by Bremner (1954), who makes it clear that although there are good grounds for the belief that a substantial part of soil organic matter is composed of lignin-derived material, the nature of its relationship to plant lignin is still very obscure. The application of the method of alkaline nitrobenzene oxidation to lignin (Freudenberg, Lautsch, and Engler, 1940) whereby good yields of phenolic aldehydes (syringaldehyde, vanillin and *p*-hydroxybenzaldehyde) can be obtained has proved of great significance in lignin chemistry. It has provided confirmation of the largely aromatic nature of the lignin nucleus or building stone (Brauns, 1952), and has shown that lignin cannot be regarded as a unique chemical compound but that the term must be applied to a group of high-molecular, chemically closely related compounds which differ according to the plant source. Gottlieb and Hendricks (1945) applied the method to soil organic matter in the hope of obtaining products which would give a clue to the chemical nature of humic substances, but in general none of the products could be identified, although in one experiment a small amount of vanillin was obtained by the oxidation of humic acid from a muck soil. Stone and Blundell (1951) described a paper-chromatographic technique for the determination of the phenolic aldehydes obtained by the nitrobenzene oxidation of lignin, and it seemed possible that further work on the application of the reaction to humic substances using such a technique for the separation of the products might yield more positive results than

had been obtained by Gottlieb and Hendricks. Preliminary qualitative experiments were encouraging and a quantitative technique was developed. While the work was in progress Bremner (1955) briefly reported the application of the technique of Stone and Blundell to soil humic acids whereby syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde were detected, but in very small yield: the maximum yield obtained, about 1 per cent., was from a peat humic acid. Detailed results are not given, but this suggests that the yields were considerably lower than those obtained in the experiments now described.

The present paper gives the yields of phenolic aldehydes obtained by the alkaline nitrobenzene oxidation of a number of soils and peats, and describes the methods used. Results are given also for a number of peat fractions which were examined in order to obtain an indication of the distribution of lignin-derived material in the fractions. In the separation of the phenolic aldehydes by paper chromatography, some disadvantages in the method of Stone and Blundell, the difficulty in maintaining the critical equilibrium in the solvent system and the necessity for running marker strips to locate the aldehydes on the paper, were avoided by the use of papers buffered at pH 10 and *tert*-amyl alcohol—pH 10 buffer solution as the solvent system. By this method it was possible to locate the aldehydes on the paper by their characteristic fluorescence in ultraviolet light. A method, similar in principle but using different buffer and solvents, has been described by Bland and Stamp (1955).

Materials and Methods

Samples. All the samples of soils, peats, and plant materials were air-dried, ground to pass a 50 B.S. mesh screen, and stored in stoppered bottles. The peat samples were all obtained from Scottish sources: Stirlingshire (Flanders West), Sutherland (Badenloch), and Aberdeenshire (Redhill *Phragmites*, Redmoss Candyglirach). Most of the soil samples were taken within 30 miles of Aberdeen, in Aberdeenshire or Kincardineshire: the exception was a manganese-deficient calcareous soil from Yambuk, Victoria, Australia.

Preparation of peat fractions. These were prepared from Redhill *Phragmites* peat. A sample (500 g.) of air-dry peat ground to pass a 50 B.S. mesh screen was extracted continuously for 16 hours with a mixture of ethanol and benzene (1 : 1 by volume). The soluble portion was taken to dryness and extracted continuously for a similar period with light petroleum (60–80° C.). The petroleum-soluble fraction (I) and the residue (II) were freed from solvent by drying in a vacuum oven at 50° C. The residue from the ethanol-benzene extraction was then suspended in 2 per cent. NaOH (30 l.) and after 24 hours with occasional stirring the dark humic-acid solution was siphoned off and the extraction with alkali was repeated; this was followed by two extractions with water. The undissolved material was collected on a Buchner filter, washed with water and dried (III). The extracts were acidified to congo red with 50 per cent. sulphuric acid and the humic precipitates were allowed to settle, washed twice with water by siphoning, and combined. The solid was freed from water as far as possible by centrifuging, and

was then frozen (Forsyth and Fraser, 1947). The cake was allowed to thaw at room temperature on a Buchner filter, and after being washed with water the humic acid was dried at 50° C. in a vacuum oven (IV). Part of this fraction was extracted continuously with ethanol-benzene (1 : 1) and divided into soluble (V) and insoluble (VI) fractions. Another portion of (IV) was boiled under reflux with 2 per cent. HCl (20 ml. per g.) for 4 hours and then filtered, washed, and dried. It was then divided by continuous extraction with ethanol-benzene into soluble (VII) and insoluble (VIII) fractions.

Organic-carbon content. The total organic carbon in the samples was determined by the wet combustion of Van Slyke and Folch (1940) as adapted by Bremner (1949).

Oxidation with alkaline nitrobenzene. The reaction vessels were stainless steel bombs (2 ml.) having screw-on caps sealed by lead gaskets (Stone and Blundell, 1951). The weighed samples (containing 20–30 mg.

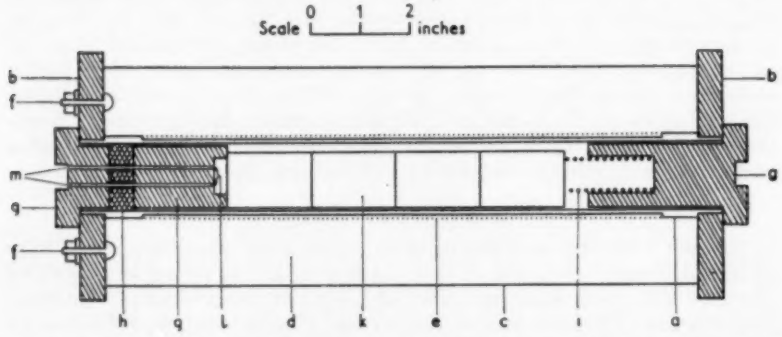

FIG. 1. Oven for alkaline nitrobenzene oxidations. *a*, iron tube; *b*, square ends of Sindanyo sheeting (Turner's Asbestos Cement Co., Manchester), connected by tie-rods at the corners; *c*, cylindrical case of aluminium; *d*, asbestos fibre packing; *e*, windings of 28 S.W.G. Nichrome, 14 turns per inch, wound round asbestos paper; *f*, terminals of winding; *g*, loose-fitting plugs of Sindanyo; *h*, iron plug screwed into tube; *i*, helical spring; *k*, bombs; *l*, copper-constantan thermocouple; *m*, leads of thermocouple. The oven is supplied with 240 volts, 1·2 amp. a.c. A Sunvic energy regulator serves to control the temperature.

of carbon) were placed in the bombs with 1 ml. of 2 N NaOH and 0·1 ml. of nitrobenzene and were heated with shaking at 170° C. for 2·5 hours in a furnace capable of carrying four bombs and designed to fit into a horizontal shaking machine. (This furnace was specially designed by Dr. V. C. Farmer and Mr. A. M. Fraser, and was constructed by the latter.) The bombs were cooled, opened, and the contents were washed out with water, diluted to 7 ml., and centrifuged. The supernatant (5 ml.) was extracted for 2 hours with ether in a continuous-extraction apparatus (Stellen and Graill, 1943). The aqueous solution was then acidified with 3 M H_3PO_4 (1 ml.) and extracted with ether for 3 hours. The ether extract was taken to dryness and the residue was transferred to a clean extraction tube with 5 ml. of 5 per cent. (w/v) $NaHCO_3$; this

solution was extracted with ether for 2 hours and the extract containing the phenolic aldehydes was evaporated to small volume and transferred to a glass-stoppered test-tube (10 × 100 mm.) by washing in with successive small quantities of ether. The ether was removed by gentle heating and the residue was dissolved in 95 per cent. ethanol (0·2 ml.).

Paper chromatography. The phenolic aldehydes were separated by partition chromatography on buffered filter paper. Strips of Whatman No. 52 paper (50 cm. × 10 cm.) were soaked in pH 10 buffer solution (50 ml. of 2 N Na_2CO_3 + 20 ml. of 0·1 N HCl, diluted to 100 ml.) and dried at room temperature (18° C.). The chromatographic solvent was redistilled technical grade *tert*-amyl alcohol saturated with the buffer solution. In this system the approximate R_F values of the aldehydes were: syringaldehyde, 0·12; vanillin, 0·20; *p*-hydroxybenzaldehyde, 0·37. Measured volumes (10–30 μl.) were applied to the baseline by means of a calibrated self-filling micro-pipette (Meinhard and Hall, 1950). The chromatograms were run for 60 hours at 18° C. by the descending method (Consden, Gordon, and Martin, 1944) and dried at 18° C. The aldehyde spots were then located by their characteristic fluorescence in ultraviolet light.

Determination of aldehydes. Portions of the paper containing the aldehyde spots were cut from the chromatograms, weighed, and placed in test-tubes (18 × 150 mm.) with 5 ml. of 0·2 N NaOH: a paper blank of similar area was treated in the same way. After 10 minutes with intermittent shaking, the optical density of the solutions was measured by means of a Beckman spectrophotometer at 365, 345, and 330 mμ for respectively syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde. A standard curve was prepared for each aldehyde from pure samples, and in each case the optical density, after correction for the blank, was found to be directly proportional to the concentration.

TABLE 1

Percentage Recovery of Aldehydes added to Samples before Oxidation

(700 μg. of each aldehyde was added to 30–50 mg. of the sample.)

Sample	*Percentage recovery*		
	Syringaldehyde	*Vanillin*	*p-hydroxybenzaldehyde*
Beech woodmeal . .	96·2	83·4	84·3
Redhill phragmites peat	55·2	79·0	73·4
Sphagnum peat . .	50·6	78·1	80·4
Craigiebuckler garden soil	46·7	82·4	82·5

Results

When known amounts of the three phenolic aldehydes were treated with the oxidation mixture in the usual way, the average recovery was 96 per cent. ranging from 91 to 102 per cent.; in the presence of beech woodmeal the recovery was somewhat lower, ranging from 83 to 96 per cent. These results accord with those of Roadhouse and MacDougall (1956) who found that in the presence of plant material added aldehydes

could not be completely recovered, and that better recoveries were obtained with mature than with young plant tissue. In the present work, the recovery of added aldehydes oxidized in the presence of peat and soil was also investigated and the results are shown in Table 1. From this it can be seen that the recoveries of vanillin and *p*-hydroxybenzaldehyde were fairly good (about 80 per cent.), but that the recovery of syringaldehyde was poor (about 50 per cent.). It should be noted, however, that the amounts of added aldehydes used in these recovery experiments were rather high in relation to the amounts normally produced by

TABLE 2

Yield of Phenolic Aldehydes from Plant Materials

Sample	*Total organic carbon (% air-dry)*	*Yield of phenolic aldehydes (% of air-dry weight)*			*Carbon in phenolic aldehydes (% of total organic carbon)*			
		Syr.	*Van.*	p-OHB	*Syr.*	*Van.*	p-OHB	*Total*
Larch woodmeal . .	46·4	nil	3·67	0·11	nil	5·05	0·16	5·21
Beech woodmeal . .	45·2	2·30	2·11	0·09	3·02	2·98	0·14	6·14
Phragmites leaves . .	41·4	1·42	1·72	0·77	2·04	2·64	1·32	6·00
Sphagnum (whole plant)	39·7	nil	nil	0·82	nil	nil	1·44	1·44

TABLE 4

Yield of Phenolic Aldehydes from Peats

Sample	*Depth (metres)*	*Total organic carbon (% air-dry)*	*Yield of phenolic aldehydes (% of air-dry sample)*			*Carbon in phenolic aldehydes (% of total organic carbon)*				*Botanical origin*
			Syr.	*Van.*	p-OHB	*Syr.*	*Van.*	p-OHB	*Total*	
Flanders West: 15	1·5–2·0	48·0	0·12	0·48	0·46	0·15	0·63	0·66	1·44	Sph.+Er.+Cal.
Flanders West: 26	7·0–7·5	45·1	1·16	1·03	0·87	1·53	1·46	1·33	4·32	Car.+Phr.
Flanders West: 32	2·5–3·0	46·5	0·34	0·55	0·58	0·43	0·76	0·86	2·05	Sph.+Er.
Flanders West: 50	5·5–6·0	46·8	0·67	1·17	0·44	0·86	1·60	0·65	2·11	Car.+Phr.+Wood
Flanders West: 193	3·5–4·0	49·3	0·38	0·83	0·58	0·45	1·07	0·80	2·32	Sph.+Er.+Cal.
Badenloch: 33 .	0·0–0·5	46·4	0·02	0·57	0·39	0·03	0·79	0·58	1·40	Sph.+Sc.
Badenloch: 61 .	1·0–1·5	48·1	0·65	0·91	0·41	0·80	1·22	0·59	2·61	Sph.+Sc.+Cal.
Redhill Phragmites	1·0–1·5	46·1	0·76	1·00	0·63	0·98	1·39	0·94	3·31	Mainly Phr.
Sphagnum peat .	unknown	42·7	0·06	0·19	0·70	0·08	0·24	1·13	1·45	Mainly Sph.

Sph. = Sphagnum, Cal. = Calluna, Er. = Eriophorum, Car. = Carex, Sc. = Scirpus, Phr. = Phragmites.

the oxidation of organic matter, and it is probable that with smaller added amounts the percentage recovery would have been reduced. This point requires investigation, but there is a distinct possibility that the potential yield of aldehydes may be higher in relation to the actual yield than these recovery figures suggest. No attempt, however, has been made to apply corrections to the results on the basis of the recoveries obtained.

In order to obtain comparable results for materials of widely divergent mineral content such as soils and peats, and in view of the difficulty of determining the total organic matter in soils, the carbon in the phenolic aldehydes has been expressed as a percentage of the total organic carbon

TABLE 3

Yield of Phenolic Aldehydes from Soils

Sample	*Total organic carbon (% air-dry)*	*Yield of phenolic aldehydes (% of air-dry sample)*			*Carbon in phenolic aldehydes (% of total organic carbon)*				*Remarks*
		Syr.	*Van.*	p-OHB	*Syr.*	*Van.*	p-OHB	*Total*	
Marsh Organic Soil (Loch of Leys, Banchory):									
0–4 in.	16·1	0·028	0·115	0·061	0·10	0·46	0·26	0·82	Mull-type, poorly drained, pH 5·7.
9–12 in.	16·8	0·033	0·139	0·068	0·11	0·53	0·28	0·92	
18–24 in.	27·0	0·206	0·333	0·126	0·45	0·79	0·32	1·56	
Dunottar Woods: 4–8 in.	2·35	+	0·021	0·009	+	0·53	0·26	0·79	Mull-type forest soil, pH 5·3.
West Fingask	4·24	0·011	0·021	0·012	0·15	0·32	0·19	0·66	Agricultural field soil.
Craigiebuckler Turf Loam	4·32	0·007	0·024	0·015	0·10	0·35	0·24	0·69	Agricultural field soil.
Craigiebuckler Garden Soil	5·38	0·030	0·056	0·025	0·33	0·66	0·32	1·31	Horticultural soil.
Pine Forest Soil Profile (Strachan):									
F_1	46·7	nil	1·90	0·19	nil	2·57	0·28	2·85	Raw humus type.
F_2	46·9	nil	1·39	0·14	nil	1·88	0·21	2·09	Pine Forest soil, pH 3·5–3·7.
H	40·8	0·10	0·71	0·12	0·15	1·10	0·20	1·45	H very thin.
A_1	13·2	nil	0·02	0·01	nil	0·10	0·05	0·15	
Yambuk (Victoria, Australia)	8·64	0·008	0·024	0·021	0·06	0·18	0·17	0·41	Poorly drained calcareous soil, pH 8·0.
Soil Humic Acid	46·3	0·051	0·249	0·122	0·07	0·36	0·18	0·61	Extracted by NaOH from Dunottar Woods Soil.

+ = present in very small amount, but not determined.

in the sample. This method of presentation eliminates differences in moisture and mineral content from the results and allows a comparison to be made between soils and peats.

The results for the oxidation of some plant materials are shown in Table 2. The results for some soils are given in Table 3 together with the results for a soil humic acid, extracted with 2 per cent. sodium

TABLE 5

Yield of Phenolic Aldehydes from Peat Profile, Redmoss, Candyglirach

Sample number	*Depth (metres)*	*Total organic carbon (% air-dry)*	*Yield of phenolic aldehydes (% of air-dry sample)*			*Carbon in phenolic aldehydes (% of total organic carbon)*				*Botanical origin*
			Syr.	*Van.*	p-OHB	*Syr.*	*Van.*	p-OHB	*Total*	
0	0–0·5	44·5	0·10	0·25	0·32	0·13	0·36	0·50	0·99	Sph. + Cal. + Er.
1	0·5–1·0	45·1	0·13	0·30	0·38	0·18	0·43	0·58	1·19	Sph.
2	1·0–1·5	45·1	0·07	0·44	0·43	0·09	0·62	0·66	1·37	Sph.
3	1·5–2·0	45·7	0·13	0·55	0·36	0·17	0·77	0·55	1·49	Sph. + Er.
4	2·0–2·5	48·8	0·24	0·81	0·26	0·29	1·07	0·37	1·73	Sph. + Er. + Cal.
5	2·5–3·0	51·7	0·09	0·79	0·27	0·10	0·97	0·36	1·43	Sph. + Er. + Cal. + Pinus
6	3·0–3·5	54·8	0·32	1·20	0·40	0·34	1·40	0·50	2·24	Er. + Cal.
7	3·5–4·0	51·4	0·88	1·75	0·60	1·02	2·18	0·80	4·00	Sc. + Bet.
8	4·0–4·5	50·2	0·66	1·58	0·48	0·78	2·01	0·66	3·45	Sc. + Bet.
9	4·5–5·0	49·2	0·47	1·27	0·38	0·57	1·65	0·53	2·75	Sc. + Bet.

Sph. = Sphagnum, Cal. = Calluna, Er. = Eriophorum, Sc. = Scirpus, Bet. = Betula.

TABLE 6

Yield of Phenolic Aldehydes from Fractions of Phragmites Peat (1·0–1·5 m.), Redhill, Aberdeenshire

Fraction number	*Total organic carbon (% air-dry)*	*Yield of phenolic aldehydes (% of air-dry sample)*			*Carbon in phenolic aldehydes (% of total organic carbon)*				*Remarks*
		Syr.	*Van.*	p-OHB	*Syr.*	*Van.*	p-OHB	*Total*	
Whole peat	46·1	0·76	1·00	0·63	0·98	1·39	0·94	3·31	..
I . .	71·4	0·03	0·95	0·11	0·03	0·85	0·11	0·99	Light petroleum-soluble.
II . .	67·9	0·85	1·06	1·33	0·74	1·00	1·35	2·09	Ethanol-benzene-soluble.
III . .	42·4	0·21	0·46	0·37	0·30	0·69	0·60	1·59	NaOH-insoluble.
IV . .	52·3	1·52	1·07	0·08	1·72	1·31	1·05	4·08	NaOH-soluble, acid-insoluble, humic acid.
V . .	60·4	3·03	2·10	1·39	2·98	2·22	1·58	6·78	Humic acid, ethanol-benzene-soluble.
VI . .	52·4	0·82	0·81	0·64	0·93	0·99	0·84	2·76	Humic acid, ethanol-benzene insoluble.
VII . .	57·2	0·68	0·56	0·66	0·71	0·63	0·79	2·13	Humic acid, HCl hydrolysed ethanol-benzene-soluble.
VIII .	54·7	0·15	0·41	0·57	0·16	0·48	0·72	1·36	Humic acid, HCl hydrolysed ethanol-benzene-insoluble.

hydroxide and precipitated with acid. Table 4 contains the results for a number of different peats with their botanical origin as indicated by microscopic examination. In Table 5 the results are given for a peat profile (Redmoss Candyglirach) sampled at 0·5-metre intervals. Table 6 contains the results obtained for the fractions prepared as described from Redhill *Phragmites* peat.

Discussion

The most important feature of the results is that they appear to provide the best evidence so far available of the presence in soil organic matter of a definite fraction of lignin-derived material.

It is clear that significant amounts of syringyl, guaiacyl, and *p*-hydroxyphenyl residues are present in the organic matter of soils and peats: the proportion varies considerably, but usually all three are present. In general there is an approximate correlation between the nature of the phenolic aldehydes obtained from the soil or peat organic matter and those obtained from the parent plant material so far as this is known. For instance, *p*-hydroxybenzaldehyde is the only aldehyde obtained by the oxidation of sphagnum (Table 2) and is the predominant aldehyde obtained by the oxidation of sphagnum peat (Table 4); the presence of other aldehydes in relatively small amount can be attributed to the fact that although sphagnum may be the dominant species contributing to the peat, other plants are always present to some extent. Similarly, as vanillin is the predominant aldehyde from the oxidation of gymnosperm lignin, so it predominates among the aldehydes from the pine forest soil samples (Table 3). In the results for the peat profile (Table 5) it can be seen that those samples in which birch remains have been detected yield relatively large quantities of syringaldehyde, as do hardwood lignins.

For soils and peats in general the carbon in the aldehydes produced on oxidation represents a smaller proportion of the total carbon in the material than it does for plant materials, and it is lower for mineral soils than for peats. This is in harmony with the belief, based on the determination of functional groups, that the degradation of lignin has proceeded farther in mineral soils than in peats (Forsyth, 1947).

There can be little doubt that the syringyl, guaiacyl, and *p*-hydroxyphenyl groups represented by the corresponding aldehydes are derived from lignin, but it cannot be said that their presence in soil organic matter indicates the presence of unmodified lignin. The manner in which these groups are built into the lignin molecule is unknown, and therefore the extent to which the lignin molecule can be modified and still yield these aldehydes on oxidation is also unknown, although experiments on model substances (Wacek and Kratzl, 1942, 1943, 1944, 1947) have indicated some possibilities. It has been found (Roadhouse and MacDougall, 1956) that acid-treated lignins give much reduced yields of aldehydes, and in the present experiments a similar effect has been observed (Table 6) where peat humic acids hydrolysed with 2 per cent. HCl gave much reduced yields of aldehydes on oxidation.

It is improbable that the yield of aldehydes represents the total content of aromatic nuclei in the organic matter. In the first place the yield of aromatic aldehydes obtained is, in view of the results of the recovery experiments, probably less than the potential, and secondly there may be aromatic groups present which are incapable of yielding aldehydes on oxidation. For example, sphagnum (Table 2) yields 0·82 per cent. of *p*-hydroxybenzaldehyde on nitrobenzene oxidation, but Farmer and Morrison (1955) obtained 4 per cent. of anisic acid by the permanganate oxidation of methylated sphagnum. Moreover, considerable amounts of unidentified aromatic material are undoubtedly present among the products of the nitrobenzene oxidation of soil organic matter.

It has been shown that certain wood-rotting fungi are capable of

attacking lignin with the production of vanillin, vanillic acid, syringaldehyde, and syringic acid (Henderson, 1955), and that numerous soil microfungi can decompose *p*-hydroxybenzaldehyde, ferulic acid, syringaldehyde, and vanillin with the rupture of the benzene ring and the production of non-aromatic substances (Henderson and Farmer, 1955). From this and other considerations it would seem unlikely that the presence of syringyl, guaiacyl, and *p*-hydroxyphenyl groups in the organic matter of well-drained mineral soils constitutes evidence of the stability of such groups. More likely it is merely further evidence of a state of dynamic equilibrium in such soils between the rates of accumulation and decomposition of lignin.

It can be seen from Table 3 that the amounts of aldehyde-forming material in the organic matter of the two field soils (West Fingask and Craigiebuckler Turf Loam) are very similar and relatively low. In the horticultural soil (Craigiebuckler Garden Soil) the proportion is considerably higher, as might be expected in a soil which receives regular heavy dressings of organic manure. In the marsh soil, although the total content of organic matter is relatively high, the proportion of aldehyde carbon is similar, but increases in the lower horizons. The organic matter in the mull forest soil (Dunottar Woods) gives a surprisingly low yield of syringaldehyde in view of the nature of the vegetation. The proportion of the total organic carbon in the aldehydes from the pine raw humus decreases down through the profile, with a very sharp drop when the A_1 horizon is reached. Syringaldehyde is usually absent and its production from the H horizon is interesting since it indicates that the organic matter here is not entirely of gymnosperm origin and may be a relic of the vegetation before the establishment of the pine forest.

It is desirable to consider the extent to which lignin in plant roots, alive at the time of sampling, might contribute to the phenolic aldehydes produced from mineral soils. Most of the soil samples were taken from sites carrying very little herbaceous vegetation, and all visible living material was removed in the course of preparing the samples. The marsh organic soil (Table 3) was exceptional in carrying a fairly heavy herbaceous growth, but, as can be seen, the yield of aldehyde increased with depth of sampling; and since the amount of fine root material would decrease with depth it can be concluded that even here such material does not make a major contribution to the aldehydes produced on oxidation.

The results for the peat profile (Table 5) indicate a tendency for the proportion of aldehyde-forming material to increase with the depth (and age) of the peat, but it is difficult to say to what extent this may be attributed to differences in the lignin content of the parent plant material or to a lower rate of decomposition of lignin-derived material relative to that of other components of the peat. In view, however, of the results of analysis of peat profiles by Waksman and Stevens (1928, 1929), who found an increase in lignin-like constituents and a decrease in cellulose and hemicelluloses with increasing depth of peat, such a tendency is to be expected.

All the peat fractions (Table 6) gave some yield of phenolic aldehyde

on oxidation, and this suggests that a wide range of lignin-degradation products is present in the peat. There is a possibility of preformed aldehydes being present in the petroleum-soluble fraction (I): Shorey (1914) isolated vanillin in small yield from a soil, and the production of vanillin and related aldehydes from wood by microbial action has been demonstrated (Sullivan, 1914; Henderson, 1955). The amount of aldehyde from this fraction is, however, small in relation to the total organic matter in the peat, and it is probable that it is either preformed or formed from related compounds of relatively low molecular weight such as ferulic acid. The relatively low yield of syringaldehyde is notable, but without obvious explanation. A higher yield of aldehydes was obtained from the ethanol-benzene-soluble fraction (II) of the original peat: this fraction could be expected to contain a rather more complex type of lignin-degradation product. The humin, or alkali-insoluble fraction of the peat (III), gave a lower yield of aldehydes than the original peat, but as the fraction is a large one this represents a high proportion of the total aldehyde-yielding material in the peat. The highest yields of aldehydes, particularly of syringaldehyde, were obtained from the humic-acid fractions (IV, V, and VI), and there was a distinct concentration of aldehyde-forming material in the ethanol-benzene-soluble fraction (V). The total humic-acid fraction (IV) is known to contain quite a high proportion of carbohydrates and amino acids, probably in the form of polysaccharides and protein (Forsyth, 1947; Bremner, 1952), and the relatively low solubility of such material in the ethanol-benzene solvent could explain the enhanced yield of aldehydes from fraction (V) and the reduced yield from fraction (VI). In the absence of other effects, however, dilute acid hydrolysis by removing sugars and amino acids could be expected to result in an increase in the proportion of aldehyde-forming material in fraction (VI), if not in fraction (V), but as can be seen the result of acid hydrolysis was a reduction in the aldehyde yield from both fractions. It follows that the dilute-acid treatment either causes the dissolution of a large part of the aldehyde-forming material or modifies it so as to render it incapable of yielding aldehydes on oxidation. The observations of Roadhouse and MacDougall on the effect of acid treatments in reducing the yield of aldehydes from plant lignins have already been mentioned.

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IDENTIFICATION OF CLAY MINERALS FROM ACID SOILS

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Summary

A technique is described for the identification of clay minerals, the layers of which are difficult to expand or collapse by the usual treatment with glycerol and KCl. Samples are extracted for 3 to 6 hours in normal sodium citrate at pH 7·3 and 100° C. The citrate is renewed hourly. After the citrate extraction the interlayer spaces of some minerals can be expanded with glycerol and $CaCl_2$.

Basal spacings of minerals previously identified as 'dioctahedral vermiculite' expand to 16–18 Å. after this treatment; hence, their identity is questioned.

The widespread occurrence in the north-eastern United States of clay minerals with 14-Å. spacing necessitates this extraction for correct identification.

AN unusual clay mineral with a basal spacing of 14 Å. has been found widely distributed in the north-eastern United States. Its behaviour resembles that of a 'dioctahedral vermiculite' found in England (Brown, 1953) and Virginia (Rich and Obenshain, 1955). The clays studied in the present work have been formed under acid conditions, a situation entirely different from the neutral or alkaline conditions often described in the literature. An analytical technique was developed to render the clays weathered under acidic conditions tractable to the classical tests of changes in interlayer spacing (MacEwan, 1949). This new technique was tested with known minerals as well as with samples of 'dioctahedral vermiculites' from three regions.

The minerals in question show properties similar to those of vermiculite, montmorillonite, and chlorite (Table 1), but do not correspond

TABLE 1

Basal Spacing of Three Established and Two Unestablished Clay Minerals after Treatment

Mineral	*Treatment*		
	Glycerol + $CaCl_2$	KCl	400° C.
Montmorillonite	18	15–10	10
Vermiculite	14	10	10
Chlorite	14	14	14
Dioctahedral Vermiculite (Brown, 1953)	14	14	11·8 (broad)
Holyoke Sample	14	14	14–10 (broad)

exactly to any one of the well-established minerals; the analytical technique was therefore modified. Brown (1953) observed a decrease of basal spacing from 14 to approximately 10 Å. when the mineral from

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England was treated in KOH+KCl for 5 hours instead of in KCl; Rich and Obenshain (1955) found that KOH+KCl or NH_4F at pH 7 produced the same collapse in the mineral from Virginia. Consequently, these workers concluded that they were dealing with dioctahedral vermiculites.

If acidic weathering has introduced interfering metal into the interlayers (Rich and Obenshain, 1955; Tamura, 1955), it should be removed. In our studies, citrate was substituted for the more destructive fluoride and hydroxyl ions and the extract examined for metal in several samples. In addition, ability to expand in glycerol was examined after removal of metal.

Materials

Samples of clays were obtained from three sources: Mr. George Brown furnished a sample containing clays which he had identified as dioctahedral vermiculite (Brown, 1953); Dr. C. I. Rich sent samples from two horizons of the Nason silt loam reported to contain dioctahedral vermiculite (Rich and Obenshain, 1955) as well as clays similar in behaviour to those reported; a sample of Holyoke stony loam from New Jersey was obtained. Vermiculite (jefferisite) from West Chester, Pennsylvania, was supplied by Professor Horace Winchell from the Brush collection of Yale University (sample No. 3779); and vermiculite from Webster, North Carolina, was donated by Dr. S. B. Hendricks.

Results

First, the behaviour of the minerals under conventional treatments was examined. Clays were segregated from five depths of the Holyoke soil, subjected to reagents and examined with X-rays. Montmorillonite was the dominant mineral present in the sample obtained at a depth of 30 to 40 in. (Table 2), as shown by the 18-Å. basal spacing after treatment with $CaCl_2$ or KCl and glycerol (MacEwan, 1944). Treatment with the NH_4F technique (Rich and Obenshain, 1955) decreased the basal spacing to 10 Å. The unknown mineral exhibiting a 14-Å. basal spacing in the upper levels also collapsed when treated with NH_4F. Treatment of the samples for 3 hours in normal potassium citrate at 100° C. left the basal spacing at 14 Å. for both the montmorillonite obtained at the 30–40-in. level and the unknown mineral with a spacing of 14 Å. found at shallower depths. Vermiculite subjected to the same treatment collapsed.

Next, the mineral's ability to expand after two methods of metal removal was determined. The first method consisted of a free-oxide removal treatment using sodium dithionite and citrate (Aguilera and Jackson, 1953). X-ray diagrams of these samples were identical with the untreated clays. The extracts were analysed for metals spectrographically and no other metals except iron and aluminium were found to be present in identifiable amounts (Table 3). Similar treatment on a Paxton soil (Tamura, 1955) had shown that if the sample is further treated with citrate only, considerable alumina is released and the Paxton clays will collapse when treated with KCl (Table 3).

Two extractions with sodium citrate without prior removal of free

TABLE 2

X-ray Diffraction Maxima for Oriented Aggregate Samples from Holyoke Soil Clays after Treatments

Treatment	Depth of samples (in.)*			
	0–4	4–16	16–30	30–40
$CaCl_2$+glycerol	..	..	18 w	18 s
	14 vs	14 vs	14 s	14 w
	10 vw	10 vw	10 w	10 w
KCl+glycerol	..	..	..	18 vw
	14 s	14 s	14 s	14 s
	..	10 vw	10 vw	10 w
KCl	14 vs	14 vs	14 vs	14 vs
	..	..	10 w	10 w
Potassium citrate	†	14 x	14 ms	14 m
	..	..	10 w	10 w
NH_4F	14 w	14–10 w (b)	†	10 ms
	12·5 m (b)			
$CaCl_2$+glycerol+400° C.	†	11·6 m (b)	10 m	10 s
Sodium citrate+$CaCl_2$+glycerol	†	18 m	18 ms	18 s
	..	14 w	14 w	..

* The 4–8 and 8–16 in. zone were very similar and therefore combined. v = very; s = strong; m = medium; w = weak; b = broad.
† Not determined.

TABLE 3

Analyses of Iron and Aluminium in Extracts from Selected Samples after Removal of Free Oxides and Treatments with Sodium Citrate

Description	Extract from samples treated*					
	For removal of free oxides (Aguilera and Jackson, 1953)		With sodium citrate after removal of free oxides		With sodium citrate only	
	Fe_2O_3 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Al_2O_3 (%)
Holyoke loam—New Jersey:						
8–16 in. $2–0·2\mu$	11·1	3·01	..	..	0·92	1·01
$<0·2\mu$	14·9	5·30	..	..	..	..
Holyoke loam—New Jersey:						
30–40 in. $2–0·2\mu$	8·46	0·95	..	..	0·68	0·05
Paxton fine sandy loam (Tamura, 1955):						
14–20 in. $2–0·2\mu$	9·39	5·14	0·0	1·09	0·90	2·10
$<0·2\mu$	12·83	8·97	0·0	1·83	0·80	3·66
Vermiculite (Webster, N.C.)	0·47	0·61	..	..	..	..
Illite (Unknown source)	0·45	0·39	..	..	..	..

* Analyses by Mr. W. T. Mathis of the Analytical Chemistry Department. No other metals were found to be present in identifiable amounts in the given extracts.

oxides contained 1·01 per cent. of alumina in the sample from 8 to 16 in. as compared with 0·05 per cent. in the montmorillonite-containing sample from 30 to 40 in. The mineral in the sample from 8 to 16 in.

when saturated with calcium and glycerol gave distinct spacings at 18 and 14 Å. Lengthening the treatment time to 3 hours resulted in a greater proportion of material converted to 18 Å. (Table 2). Longer heating periods did not appear to increase the 18-Å. component. The X-ray diagram of the sample at 8–16 in. is reproduced in Fig. 1 to

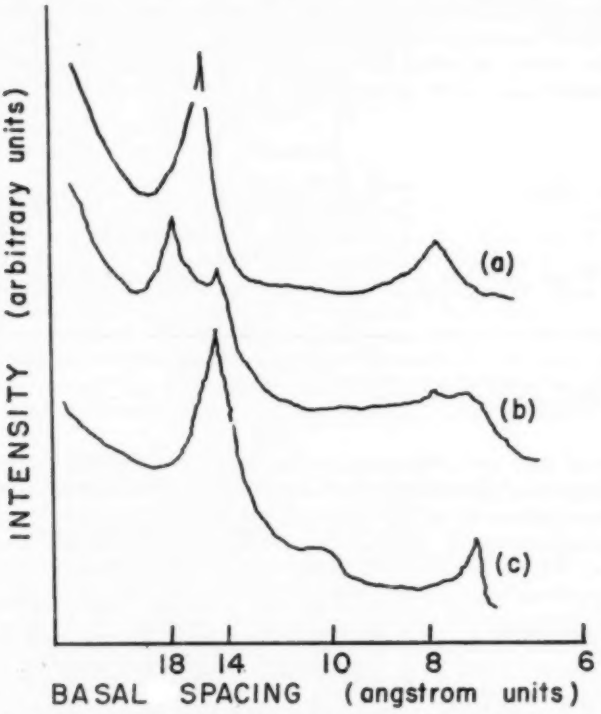

FIG. 1. X-ray diffraction patterns of oriented aggregate samples of (*a*) jefferisite, (*b*) Holyoke soil clay from a depth of 8–16 in. after extraction with citrate and treatment with glycerol and $CaCl_2$, and (*c*) similar to (*b*) except that extraction was omitted.

show the magnitude of change. In contrast to this, the spacing of vermiculites treated with citrate for as long as 12 hours, and then with $CaCl_2$ and glycerol, remained at 15·5 Å. Fig. 1 records the response of jefferisite treated for 12 hours in citrate. The 15·5-Å. spacing observed in the vermiculites is near the 15·05 Å. reported (Barshad, 1948) for calcium-saturated vermiculite; the difference is probably due to glycerol since the unheated vermiculites also showed spacings of 15·5 Å. Obviously the citrate treatment followed by glycerol and $CaCl_2$ causes the unknown Holyoke but not the vermiculite clays to expand. The treatment consisted of heating the clays for 3 hours in normal sodium citrate (pH 7·3)

at 100° C. Ten ml. of citrate solution was used for each 50 mg. of clay and the citrate solution was renewed hourly after centrifugation and decantation.

From the data in Table 3, the important role of aluminium in preventing expansion is evident. Not only was it necessary to remove a considerable amount of alumina to achieve expansion but the initially high free-iron-oxide content in the sample from 30 to 40 in. did not prevent the montmorillonite from expanding. Although a large quantity of alumina was removed by the method of Aguilera and Jackson (1953), no expansion of the 14-Å. mineral was observed. The alumina extracted by their treatment may originate from alumino-silicates (allophane type) which are soluble in the presence of dithionite but not citrate. An account of the effect of acid weathering on north-eastern soils as related to clay decomposition will be published elsewhere.

The results of these tests show that the interlayer metals are capable of preventing expansion of clay minerals. Since earlier workers (Brown, 1953; Rich and Obenshain, 1955) did not test for expansion after treatment with KOH+KCl and NH_4F, their samples were treated with citrate and then $CaCl_2$ and glycerol. Expansion was a function of time and sample: the samples from the upper horizons and from England

TABLE 4

*X-ray Diffraction Maxima for Oriented Aggregate Clay Samples from Virginian and English Soils**

Source	*Horizon and depth*	*Extraction (hours)*	*Diffraction maxima*	*Remarks*
Nason silt loam, Fluvanna County, Virginia	B_1 9–13 in.	0	14·5 s	
		3	17·0 s	
		6	17·0 s	
	B_2 22–36 in.	0	17·0 w	
			14·7 s	
			17·0 s	
		3	14·7 vw	
		6	17·0 s	
Nason silt loam, Louisana County, Virginia	B_1 10–14 in.	0	14·2 s	
			17·0 s	Sharp 17·0 maximum 'tailing' to 14·7.
		3	14·7 w	
		6	17·0 s	
	C_2 54–62 in.	0	17·0 m	Sharp 17·0 maximum 'tailing' to 14·7.
			14·5 w	
		3	17·0 s	
		6	17·0 s	
Moses Cocker's farm, Lancashire, England	.. 3½–9 in.	0	14·7 s	
		3	16·4 m	Broad pattern ranging from 17·7 to 15·2.
		6	16·7 m.	Broad pattern ranging from 17·7 to 16·0.

* Maxima are given in Å. for basal spacing. Extraction was at 100° C. in normal sodium citrate. Following extraction samples were treated with glycerol and $CaCl_2$. Intensity abbreviations are defined in Table 2.

not only required longer extractions with citrate for expansion but expanded less (Table 4).

Since it is possible that minerals with 14-Å. basal spacings could undergo similar acidic reactions, samples which were previously identified as vermiculite were subjected to the citrate treatment. Two samples from a Paxton soil in Connecticut are of interest. The two samples selected represent the D and B_{22} horizons; the mineralogical analyses were published earlier (Tamura, 1955). The D horizon contained an interstratified vermiculite-mica mineral whose X-ray pattern showed a maximum at 11·6 Å. The trioctahedral character and decrease in spacing with KCl treatment (Barshad, 1948) of the D-horizon sample strongly suggest vermiculite as the expanded component. The B_{22} sample exhibited maxima at 14·2 and 12·3 Å. with calcium saturation; no significant change in spacing was noted after KCl treatment. These samples when treated for 3 hours with sodium citrate after removal of free oxide did not show changes in the diffraction patterns when treated with glycerol; when saturated with KCl after the citrate treatment, the spacing was reduced to 10·5 Å. in the B_{22} clay sample.

Discussion

The value of chemical treatments to alter interlayer spacing is well established in clay-mineral identifications. Barshad introduced salted pastes to reveal spacings not before detected (Barshad, 1954). Brown (1953) employed KOH to collapse layers unaffected by KCl. Chlorites from Lorraine iron ore were extracted with complexing agents to transform them into nontronites, and the 'expanding chlorites' from the Keuper Marl appeared as a mixture of montmorillonite and mica after treatment with HCl (Caillère *et al.*, 1954). Therefore the citrate extraction developed here is one of a large group of similar and useful techniques valuable in the taxonomy of clay minerals.

What new information does this technique provide concerning the nature of the unknown mineral in the English sample and in the upper horizons of the samples from the north-eastern United States? First, extraction with a metal complexing agent that is non-destructive to the mineral does not cause either the unknown mineral or montmorillonite to collapse like vermiculite when potassium is added. Second, extraction by a method that removes iron and, especially, aluminium permits the unknown mineral and montmorillonite, but not vermiculites, to expand when glycerol and $CaCl_2$ are added. Third, the extraction causes the unknown mineral in the upper horizons of Virginia and New Jersey soils to behave like the montmorillonite in the lower horizons. These three observations lead to the conclusion that the unknown mineral is of a montmorillonite type, modified by weathering under acidic conditions.

The failure of the English sample to expand fully to 17–18 Å. may be due to insufficient time allowed for removal of metal. This view is supported by the character of the diffraction diagram. Thus, heating for 3 hours revealed spacings ranging from 15·2 to 17·7 Å. with the maximum

at 16·4 Å.; heating for 6 hours decreased the range of spacing to 16·0–17·7 Å. with the maximum increased to 16·7 Å. Investigation of samples from greater depths would probably be of value in elucidating the genetic relationship of the 14-Å. clay.

The behaviour of the English sample after treatment with the citrate solution would lead one to suspect occurrence of clays which may be even more difficult to expand; and conversely samples of clays may be found which are easier to expand. Thus, in the light of new evidence, the clay reported in a Wethersfield soil (Tamura and Swanson, 1954) can be shown to be montmorillonite with metals in interlayer positions. The partial expansion without citrate treatment ranging from 18 to 14 Å. in the C_1 horizon is evidence of 'loosely bound' plates of montmorillonite in contrast to the more 'tightly bound' plates of the English sample which required prolonged citrate treatment. Three hours extraction in citrate resulted in most of the clay being expanded to 18 Å. in the Wethersfield clay.

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GRASS OPAL IN BRITISH SOILS

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WITH ONE PLATE

Previous Pedological and Botanical Work

THE fact that certain small particles of opaline silica present in the soil are derived from plants has long been recognized by Russian pedologists. Tyurin (1937) gave drawings of such bodies present in the sedge *Carex gracilis*, in the reeds *Phalaris arundinacea* and *Phragmites communis*, and also in Russian soils. He refers to a paper by Ruprecht (1866) in which these bodies are already referred to as phytoliths[1] and are recognized in the grass *Stipa pennata* and in chernozem, particularly in the topsoil. More recent Russian work indicates continued interest in these objects (Usov, 1943; Parfenova, 1956; Yarilova, 1956; Parfenova and Yarilova, 1956).

The most comprehensive general account of the methods and results of studying silica bodies in plants is that of Netolitsky (1929) who gives an extensive bibliography extending back to the work of Struve (1835). The specialized account of the morphology of grasses by Prat (1931) gives much information on the occurrence of silica. Nevertheless, when an attempt is made to match the soil opal particles with those in the grass, the botanical literature affords no substitute for direct observations on the grasses growing on the site.

Methods of the Present Investigation

Selection of sites. The occurrence of opal of plant origin in British soils has been noted by the writer (Smithson, 1956*a*, 1956*b*). This and subsequent work suggested that opal particles occur widely in Britain and come mainly from members of the grass family. As cereals are well known to secrete silica, it was thought that a study of the plots at Rothamsted which have been under these crops continuously for over a century might yield interesting accumulations in spite of the fact that the major part of the crops is harvested. Samples from the Broadbalk wheat plots on the whole gave a poor yield of opal particles although they were moderately common in the plot which had regularly received farmyard manure. The same was true of the Hoosfield barley plots. In the part of the Broadbalk wilderness which has remained under grass, the bodies were more plentiful. Some of the richest accumulations, however, have been encountered in grazing land in North Wales, and in some of these the evidence that most of the soil opal came from the grass leaves

[1] The term phytolith, implying the stony part of a plant, appears to be used only for bodies which are minute parts of the plants which secrete them. It is not applied to diatom skeletons where the secretion is the full size of the organism. Though the term might logically be used for any mineral substance secreted by a plant (e.g. calcium carbonate in *Chara*), in all the cases dealt with in the present paper the material is opal, $SiO_2.nH_2O$.

is very convincing. For convenience a number of types of grazing land near Bangor were studied and three examples were selected for detailed description because they fulfil the following conditions:

(i) Although there is no written record, the vegetation is such that it can be assumed to have remained unchanged for a long period, so that the grass species now dominant are likely to have supplied most of the phytoliths found in the soil.

(ii) The number of species of grasses is not very large.

(iii) Some of the grasses at each locality yield phytoliths with peculiarities of shape or ornamentation which help one to recognize them when they are preserved in the soil.

(iv) Phytoliths are abundant in the topsoil and are less affected by corrosion than in many of the other soils examined.

Treatment of soils. If a soil is treated by standard methods for mechanical analysis, microscopic examination may show that some of the larger particles of the silt fraction (2 to 20 μ) and some of the smaller ones of the fine sand (20 to 200 μ) are phytoliths, so that to obtain a single concentrate containing all of these objects it is necessary to select non-standard size limits. Suitable settling times may be found by experiment for a particular sample, but a change of $\times 10$ in the standard time, i.e. of $\times \sqrt{10}$ in the nominal size limits to approximately 6·3 to 63 μ, should generally be satisfactory. Although the hydrogen-peroxide treatment will have cleaned the material, further improvement is obtained by heating with concentrated chromic acid. Moreover, if microscopic examination of the smaller phytoliths with an oil-immersion objective is to be undertaken further fractionation is desirable, otherwise the objects may lie below the level of focus when mounted.

The process of panning, as used in gold prospecting and in the laboratory study of heavy minerals, can be used to pan off the rod-like opal particles. An electric vibrator, as used for electric massage, applied to the wet silt in a basin is effective in bringing these particles to the surface. Attempts to concentrate the opal by a heavy liquid (sp. gr. *c.* 2·3) have been successful in separating opal (*c.* 2·1) from quartz (*c.* 2·6) in the fine sand, but in the case of silt the method has been less satisfactory.

Treatment of grasses. In ordinary botanical preparations the presence of phytoliths often escapes notice, or if the phytoliths are seen they are all viewed from the same aspect so that the complexities of their shapes are not fully realized. It is not until the organic matter has been destroyed by oxidation that they are seen to full advantage. For oxidation by burning, the plant material should be treated with dilute hydrochloric acid and soaked in several changes of boiling distilled water, dried in an oven, and then set alight in a large crucible. When combustion ceases the black mass which remains is covered with a lid which will admit air and yet prevent loss of ash by convection currents as the final stage of combustion is completed by heating with a bunsen burner. Oxidation by hot concentrated chromic acid is another well-established method for destroying the organic matter, but the subsequent washing and mounting of the insoluble residue is troublesome. Both these

drastic oxidation methods may completely detach the phytoliths or may leave small groups of them held together by only a thin film of silica.

In work on grass leaves (Parry and Smithson, 1957) it has been found that better results are obtained by warming with a mild oxidizing agent (e.g. hydrogen peroxide) and following this by warming in dilute chromic acid. By careful manipulative methods, details of which it is proposed to publish elsewhere, preparations are obtained with the silica particles in their correct relative positions. Results may be spoiled by charring when the chromic acid is applied unless a little nitric acid is also present.

Treatment of dung. The droppings of the animals grazing on the sites were collected and treated first with hydrogen peroxide and then with concentrated chromic acid. Sedimentation was necessary to remove some relatively large mineral grains, mostly quartz, which were most numerous in the cattle dung.

Microscopic examination. Soil, plant, and dung preparations were examined to detect opal and make scale drawings, using a microscope with polarizing and phase-contrast equipment and a camera lucida. Using ordinary illumination and having Canada balsam or methyl salicylate as the medium, quartz is inconspicuous but opal stands out boldly (refractive indices: Canada balsam, methyl salicylate and quartz, *c.* 1·54; opal *c.* 1·43). Using a phase-contrast objective and a glycerine-water medium of refractive index *c.* 1·42 the opaline bodies are seen clearly when the substage annulus is in position, but become almost invisible when it is withdrawn.

TABLE 1

Data for the Selected Localities

The classification of the grasses follows Hubbard (1954).

	Grasses studied
A. Rough enclosed pasture for cattle and sheep, about 300 ft. above sea level, near Menai Bridge, Anglesey. Grid reference 23/555740	Festuceae *Cynosurus cristatus* *Poa annua* *Dactylis glomerata* Aveneae *Anthoxanthum odoratum* *Holcus lanatus* Agrosteae *Agrostis tenuis*
B. Rough open pasture for sheep, 1,700 to 1,800 ft. above sea level, near Aber, Caernarvonshire. Grid reference 23/700710	Festuceae *Festuca ovina* Nardeae *Nardus stricta*
C. Rough enclosed pasture for ponies, very wet, about 350 ft. above sea level, near Pentir, Caernarvonshire. Grid reference 23/560680	Danthonieae *Molinia caerulea* *Sieglingia decumbens*

Opal, being isotropic, becomes dark and hence invisible when the polars are crossed at 90°, but if one of them is set at about 10° from its normal position the opal appears grey in a grey field, and if the medium is Canada balsam or methyl salicylate the boldness of outline and

characteristic shapes as well as the isotropism can be observed at one glance.

If the soil preparation is examined in a bromoform-tetralin mixture of specific gravity *c.* 2·4, opal floats into contact with the cover-glass while other minerals present rest on the slide, so that when the opal is seen clearly the other minerals are out of focus.

Description of the Phytoliths

Details of the three localities and of the list of grasses studied are given in Table 1.

Locality A. The opal particles in the soil, leaf blades, and dung are mostly unbranched rods, either plain or ornamented. The plain rods found in the soil may be from the leaves of *Anthoxanthum odoratum* and *Holcus lanatus* (Fig. 1, nos. 1–5 and 28–33; Plate D), but plain rods were also obtained by treating a culm of *Cynosurus cristatus*. The ornamented forms would appear to offer a better chance of matching.

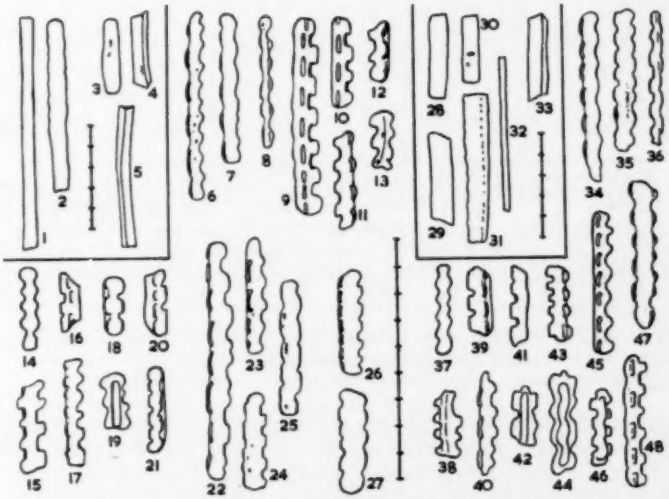

FIG. 1. Phytoliths from grass leaves and soils at locality A. Magnifications are indicated by scales graduated at intervals of 10 μ.

1 and 2, *Anthoxanthum odoratum*; 3–5, *Holcus lanatus*; 6–13, *Agrostis tenuis*; 14–21, *Cynosurus cristatus*; 22–25, *Poa annua*; 26 and 27, *Dactylis glomerata*; 28–48, Topsoil samples.

These bodies lie along or parallel to the ribs of the leaf, and where they can be seen in an ordinary epidermal preparation they appear as rods with wavy edges. With chromic-acid treatment, however, they may be accidentally thrown into many different orientations (Pl. I, E and F), so that they appear to be boat-shaped objects with clefts along the sides and at the ends. This disturbance of the phytoliths is an advantage for it allows them to be compared in various orientations with the particles

seen in soil preparations (Fig. 1, nos. 6–27 and 34–48; Pl. I, A). The two dominant grasses supplying bodies of this type to these soils are *Agrostis tenuis* and *Cynosurus cristatus*, but as some other grasses (e.g. *Poa annua* and *Dactylis glomerata*) occurring less commonly at this locality contain similarly shaped bodies it may be unwise to do more than attribute these forms to an assemblage of grasses covering more than one tribe.

Bodies of other shapes occur in the leaves of these grasses, but they are less abundant and less distinctive than those shown in the illustrations.

In the wetter parts of the pastures some *Sieglingia decumbens* is present and has contributed to the soil silica, but this species is dealt with fully in the description of locality C.

Locality B. In this mountain pasture sampling was carried out at points where *Nardus stricta* and *Festuca ovina* were the dominant grasses, but as the sheep were free to wander over some miles of country

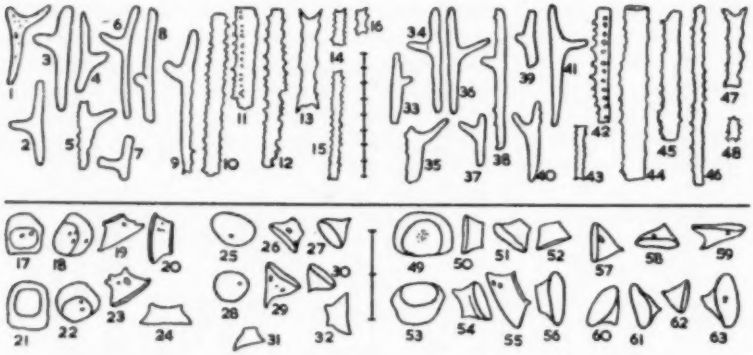

FIG. 2. Phytoliths from grass leaves and soils at locality B. Magnifications are indicated by scales graduated at intervals of 10 μ
1–24, *Nardus stricta*; 25–32, *Festuca ovina*; 33–63, Topsoil samples.

in parts of which *Agrostis spp.* are also common, it is not surprising that many 'wavy-edged' rods were found in the dung and that they were also present in the soil. Nevertheless, a large proportion of the larger opal particles observed in the soil samples are branched and prickly rods clearly attributable to *Nardus stricta*, the only British member of the tribe Nardeae (Fig. 2, nos. 1–16 and 33–48; Pl. I, B). Much smaller hat-shaped bodies are also found in the leaf of this grass and bodies which match them are also present in the soil (Fig. 2, nos. 17–24 and 49–56). In *Festuca ovina* no rods were observed, but an abundance of minute bodies are present. When they can be seen undisturbed in the leaf preparation they appear as round bodies, but when they have become scattered they are seen to be hat-shaped, but unlike the small bodies in *Nardus* they commonly taper to a single point. Bodies which match these are also found in the soil (Fig. 2, nos. 25–32 and 57–63). Their abundance in the sheep dung confirms that this is the animal's favourite diet.

Locality C. On this wet pasture there is an abundance of the only two British members of the grass tribe Danthonieae, namely *Molinia caerulea* and *Sieglingia decumbens*. In both, several types of phytoliths are present, for example:

(*a*) Relatively large rectangular plates with ribbing parallel to the edges (Fig. 3, nos. 1–3 and 11; Pl. I, H).

(*b*) Thick fan-shaped bodies (Fig. 3, nos. 4 and 12–14).

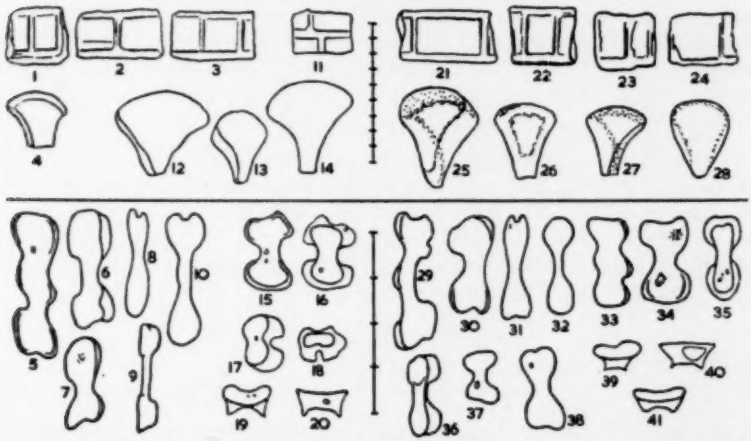

FIG. 3. Phytoliths from grass leaves and soils at locality C. Magnifications are indicated by scales graduated at intervals of 10 μ
1–10, *Molinia caerulea*; 11–20, *Sieglingia decumbens*; 21–41, Topsoil samples.

(*c*) A type abundant in both species and usually described as 'dumb-bells' (Fig. 3, nos. 5–10 and 15–17; Pl. I, G and I–M), although in *Molinia* they may bulge in the middle as well as at the ends (e.g. no. 5) and in general when they are turned on edge they assume a very different appearance (Pl. I, L and M).

(*d*) Small bodies which are very common in *Sieglingia*, lying between the lines of 'dumb-bells' (Fig. 3, nos. 18–20; Pl. I, I and J) and somewhat resembling the hat-like bodies of *Nardus* and *Festuca ovina*.

All these forms can be recognized in the soils at these sites (Fig. 3, nos. 21–41; Pl. I, C). Some can confidently be identified as belonging to *Molinia* and others to *Sieglingia*, but in some cases it is not possible to decide which of these grasses is the source. At locality A, where *Sieglingia* is present and *Molinia* absent, the 'dumb-bells' found in the soil are presumed to be derived from the former, since no other grasses on the site appear to contain such bodies.

Conclusion

Evidence has been presented to show that the leaves of grasses can contribute to the soil vast numbers of opal particles of 'coarse silt' and

'very fine sand' size. The culm and the flower-head of the grass appear to make a smaller contribution, but no evidence has been found that the roots are a source of any opal particles. *Nardus stricta*, a grass with no close relatives in Britain, contains phytoliths which could not be mistaken for those from any other of the grasses encountered in the present work. Usually the soil phytoliths can be assigned much less definitely, e.g. to one grass tribe, or to a group of tribes. The presence of phytoliths in the dung of grazing animals shows that these bodies must be distributed to some extent by the movement of animals and by the application of farmyard manure to crops. Some phytoliths in soils are pitted and corroded to a degree apparently dependent on their age and on soil conditions.

Acknowledgements

The writer is grateful to Dr. A. Muir for making it possible to collect samples of Rothamsted soil, and for drawing attention to some of the Russian literature. Thanks are also due to colleagues at Bangor—Mr. D. Wynn Parry for guidance on the botanical side of this work, Mr. R. I. Davies for discussions on the pedological aspects, and Dr. C. B. Coulson for translating from the Russian.

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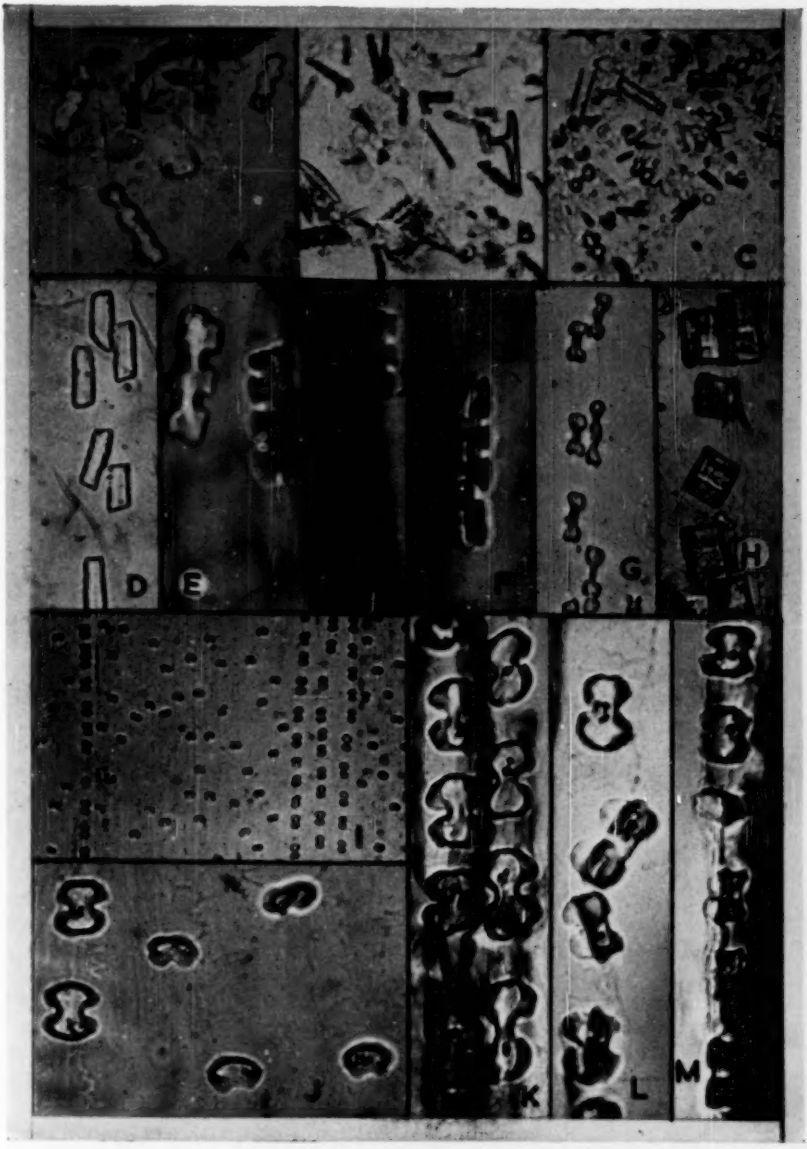
(*Received 1 May 1957*)



All preparations are mounted in Canada balsam

Opaline silica bodies in North Wales soils:

A, B, and C. From localities A, B, C. ×370, ×180, ×280.

Opaline bodies from grass leaves treated with dilute chromic acid:

D. *Holcus lanatus*. ×330.

E, F. *Cynosurus cristatus*. ×660, ×850.

G, H. *Molinia caerulea*. ×280, ×180.

I–M. *Sieglingia decumbens* (I, ×140; J, ×660; K–M, ×680)

F. SMITHSON—PLATE I

THE EFFECT OF NITROGEN ADDITIONS ON FERTILIZER-PHOSPHORUS AVAILABILITY. II[1]

D. A. RENNIE AND R. J. SOPER[2]
(University of Saskatchewan, Saskatoon, Saskatchewan)

Summary

A field and greenhouse study has been made of the effect of nitrogen on the utilization of fertilizer phosphorus by cereal grains. A marked increase in utilization when nitrogen was mixed with either $NH_4H_2PO_4$ or $Ca(H_2PO_4)_2$ was shown to occur only when the nitrogen was in the ammonium form. Nitrate sources of nitrogen were relatively ineffective. Placement of nitrogen was important as increased uptake only occurred when the ammonium ion was intimately associated with the phosphorus fertilizer. This stimulative effect of the ammonium ion on phosphorus uptake occurred at a very early stage of crop growth.

Rapid ammonium-ion absorption by young cereal seedlings occurred irrespective of whether the ammonium source of nitrogen was mixed with, or separated from, the phosphorus carrier. Thus the ammonium ion appears to be the dominant factor; it indirectly influences the plant's ability to take up phosphorus, rather than altering in any way the availability of the applied phosphorus fertilizer.

Introduction

THE role of nitrogen in promoting fertilizer phosphorus utilization by cereal grains grown under differing soil and climatic conditions was reported in 1954 (Rennie and Mitchell). At that time, it was suggested that the uptake of phosphorus from the fertilizer may have been increased due to the increased acidity that would develop in the fertilizer band as the ammonium ions in the ammonium nitrate, or ammonium sulphate, were oxidized to nitrates. This increased acidity would probably reduce the rate of fixation of the fertilizer phosphorus. This reasoning was based on previous work carried out by Mitchell *et al.* (1952), who had shown that small additions of elemental sulphur could greatly increase the availability of phosphorus in a fertilizer such as dicalcium phosphate which otherwise gave poor availability in soils of high base status in Saskatchewan.

Further evaluations of the interaction between nitrogen and phosphorus uptake by cereal grains are included in this study. An attempt was also made to determine whether the acidulation effect of the ammonium salts provided a satisfactory explanation for the marked increase in the utilization of fertilizer phosphorus when the phosphorus carrier was mixed with an ammonium source of nitrogen.

Laboratory Procedures

The active mono-ammonium and mono-calcium phosphate used in the field trials was supplied by the Plant Industry Branch, United States

[1] Contribution from the Department of Soil Science, University of Saskatchewan, Saskatoon, Sask. Part of a thesis presented by R. J. Soper in partial fulfilment of the requirements for the degree of Master of Science, University of Saskatchewan.

[2] Assistant Professor and Research Assistant respectively.

Department of Agriculture, Beltsville, Maryland. The specific activity of the tagged fertilizers was approximately 150 μC P^{32} per gramme P^{31} at seeding time. Radioactive phosphorus used in greenhouse experiments was obtained from Atomic Energy of Canada, Ltd. It was added in the form of H_3PO_4 to a solution of an inactive phosphorus carrier to give an activity level of approximately 200 μC P^{32} per gramme P^{31}. The tagged fertilizer was applied either in solution or in a crystalline form following evaporation to dryness at 30° C.

The P^{32} radioanalysis of the dried, threshed, and ground grain samples, was carried out according to the method outlined by Kristjanson *et al.* (1951). Where samples were taken prior to maturity, the oven-dry plant material was wet-ashed and counted in solution (Veall, 1948). All samples were counted for sufficiently long to reduce the counting error to less than 1 per cent.

For total analysis, the grain and forage samples were wet-ashed by the method of Brenner and Harris (1939) and phosphorus determined by the metavanadate method (Kitson and Mellon, 1947).

Nitrogen was determined on a semi-micro basis using a distillation apparatus similar to that described by Markham (1942).

Since field and greenhouse techniques varied with different tests, they are described together with the results obtained from each individual experiment.

Results

Nitrogen and phosphorus uptake

Further evaluation of the effect of nitrogen on phosphorus uptake was obtained in 1954. Two locations were selected on the same soil type, Melfort silty clay loam,[1] a thick, black, neutral to slightly acid soil developed on heavy glacial lacustrine deposits. Plots were laid down on fallow, where no nitrogen deficiency was expected, and on stubble land where rather large yield increases might be expected due to additional nitrogen fertilization. The plots were laid out in a 6×6 repeated lattice design using thirty-six treatments and six replicates (Clem and Federer, 1950). Identical treatments of varying rates of $NH_4H_2PO_4$ and $CaH_4(PO_4)_2$ to which increasing amounts of NH_4NO_3 were added were tested at both sites. The levels of P_2O_5 and N used are shown in Tables 1 and 2. When adding NH_4NO_3 to $NH_4H_2PO_4$ the amount was reduced by the amount of N already present in this phosphorus carrier. Thatcher wheat was used as the test crop. Both fertilizer and seed were applied together, using a specially constructed power seeder. Each treatment consisted of a central row fertilized with active fertilizer and two adjacent guard rows which were given the same fertilizer treatment using inactive fertilizer. The plots were harvested at maturity, dried, and threshed to obtain the weight of grain.

The grain yields obtained on the fallow and stubble plots are given in Table 1. Yields of grain show good response to phosphorus fertilization on fallow land, but nitrogen, regardless of rate, has had no effect on

[1] A complete description of this soil can be found in Saskatchewan Soil Survey Report No. 12, 1944, Department of Soil Science, University of Saskatchewan, Saskatoon, Saskatchewan.

yield. On the stubble plot, larger responses to phosphorus fertilization were obtained when nitrogen was added with the phosphorus. With adequate nitrogen and phosphorus, the yield on this stubble plot was almost doubled. The data obtained on both plots for the $NH_4H_2PO_4$ treatments have been omitted, as yield variations due to nitrogen additions were similar to those obtained using $CaH_4(PO_4)_2$.

TABLE 1

Effect of Nitrogen (NH_4NO_3) *and Phosphorus* ($CaH_4(PO_4)_2$) *Fertilization on the Yield of Wheat (Bushels per Acre)*

Lb. per acre of N *as* NH_4NO_3	*Lb.* P_2O_5 *per acre as* $CaH_4(PO_4)_2$							
	0	6	12	24	0	6	12	24
	Fallow				Stubble			
0	41·6	49·2	53·0	54·5	20·0	22·4	25·1	24·0
10	40·6	49·4	54·0	52·1	19·8	25·8	27·2	26·2
20	41·2	48·1	51·8	51·5	24·3	28·8	29·4	28·8
40	46·2	49·4	51·0	54·5	26·2	29·9	33·3	35·4
L.S.D. (P = 0·05)	5·0	..	..	..	3·8	..	..	..

TABLE 2

A Comparison of 'A' Values Obtained using Varying Rates of Application of $CaH_4(PO_4)_2$ *to which Increasing Amounts of* NH_4NO_3 *were Added*

Lb. per acre of N *as* NH_4NO_3	*Lb.* P_2O_5 *per acre as* $CaH_4(PO_4)_2$					
	6	12	24	6	12	24
	Fallow			Stubble		
0	65	69	70	103	106	151
10	65	68	58	67	79	81
20	59	53	59	54	56	72
40	56	53	49	55	49	53
L.S.D. (P = 0·05)	10	..	..	18·6	..	..

The uptake of fertilizer phosphorus and calculated 'A' values for the respective treatments are given in Fig. 1 and Table 2. On the fallow plot, the addition of NH_4NO_3 to either $NH_4H_2PO_4$ or $CaH_4(PO_4)_2$ has increased the utilization of the applied phosphorus. This increased utilization of fertilizer phosphorus by the plant was usually accompanied by a drop in 'A' values (soil phosphorus uptake either remained constant or decreased).

The 'A' values on the fallow plot, given for the various phosphorus treatments, behave in the usual manner. At any one level of nitrogen, 'A' values did not change with increasing applications of P_2O_5. This is in contrast to the gradual reduction in 'A' values with increasing applications of nitrogen to the phosphorus carrier. Since there is little evidence to suggest that soil phosphorus availability has been altered, it would appear that the nitrogen has changed the characteristics of the fertilizer in such a manner as to make it more available to the plant.

These data are in accordance with previous observations (Mitchell, 1946) that the $CaH_4(PO_4)_2$ is not as efficient as $NH_4H_2PO_4$ as a source of phosphorus for wheat on the soils of Saskatchewan. Differences between the fertilizer uptake values for the two phosphorus carriers are not great, however, and significant differences were consistent only where the carriers were applied at 24 lb. of P_2O_5 per acre. The average percentage utilization of the applied fertilizer for all treatments is 33·7 per cent. for

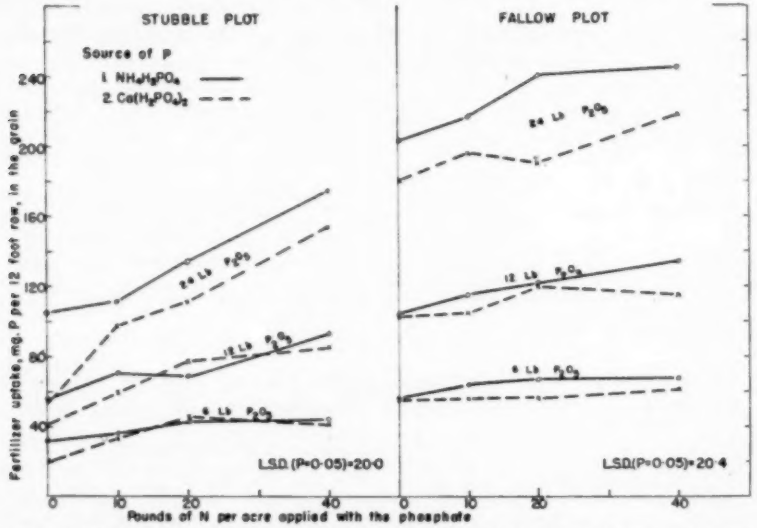


FIG. 1. Fertilizer phosphate uptake by wheat fertilized with mono-calcium and mono-ammonium phosphate to which increasing amounts of ammonium nitrate were added. Identical treatments were laid on fallow and stubble Melfort silty clay loam.

the $CaH_4(PO_4)_2$ and 37 per cent. for the $NH_4H_2PO_4$. It is evident from the curves plotted in Fig. 1 that the addition of NH_4NO_3 to $CaH_4(PO_4)_2$ does not exert quite as marked an effect on uptake by wheat as its addition to $NH_4H_2PO_4$. This would suggest that the effect of the calcium ion in reducing the availability of a phosphorus carrier cannot be entirely overcome by the addition of nitrogen.

The effect of fertilizer nitrogen in stimulating plant use of fertilizer phosphorus is more clearly manifested throughout the stubble-plot data. The phenomenon is, however, complicated by the nutritional response which was obtained from the applied nitrogen. It is impossible to separate that portion of the increase utilization which was obtained due to the additional growth brought about by overcoming a nitrogen deficiency in the soil, from that due to the indirect effect observed on the fallow plot. These data illustrate the danger of attributing the effect of the added nitrogen to some 'unknown' mechanism where a deficiency of nitrogen exists in the soil. It is to be expected that a larger, more thriving plant would naturally utilize more applied fertilizer phosphorus.

Nitrogen placement studies

A portion of the data obtained on placement studies was obtained from field plots on fallow Melfort silty clay loam. Nitrogen, as NH_4NO_3, was applied at 20 and 40 lb. of N per acre: (1) as a top-dressing treatment immediately after seeding, the phosphorus ($CaH_4(PO_4)_2$) being applied at 25 lb. of P_2O_5 per acre with the seed, and (2) together with the phosphorus in the manner previously outlined.

The fertilizer-uptake data and 'A' values are illustrated in Fig. 2.

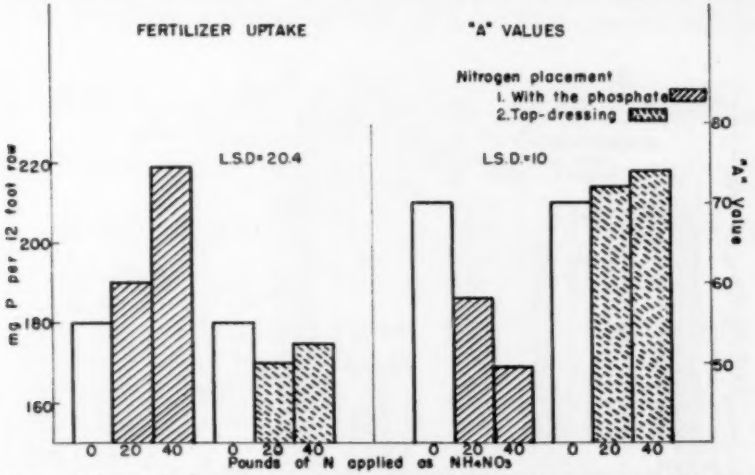


FIG. 2. Effect of nitrogen placement on uptake of fertilizer phosphorus and 'A' values of wheat grown on Melfort silty clay loam.

The top-dressing nitrogen treatments have not, in any instance, significantly altered the amount of phosphorus absorbed from the fertilizer, nor changed the 'A' values, while the usual marked role of nitrogen in promoting fertilizer phosphorus uptake is apparent where the nitrogen and phosphorus were placed together with the seed.

Greenhouse experiments conducted in the spring and fall of 1954, which will be designated 'A' and 'B' respectively, further illustrate the importance of placement of the nitrogen fertilizer with respect to the phosphorus carrier. In both cases barley was grown in 5 lb. of Elstow silt loam soil[1] in glazed half-gallon crocks. $NH_4H_2PO_4$ and $(NH_4)_2SO_4$ were used as phosphorus and nitrogen sources. All treatments received an application of 24 lb. of P_2O_5 per acre. In experiment A, the nitrogen was applied at a rate of 50 lb. per acre in two ways, namely, mixed with the phosphorus and applied at seed level; and mixed with the top 4 in. of soil, the phosphorus only being applied with the seed. The plants were harvested at the late-dough stage. In experiment B, the fertilizer was applied in solution after the plants had reached the second-leaf stage. This was done by taking out three cores of soil

[1] See note on p. 156.

2 in. in length and pipetting 5 ml. of solution into the bottom of the core. The core was then replaced. In the treatment where the nitrogen was added separately from the phosphorus, six cores were removed, the phosphorus being placed in three of these and the nitrogen in the other three. The crop was harvested at two stages of growth, 15 and 27 days after adding the fertilizer.

The uptake of fertilizer phosphorus and calculated 'A' values for both

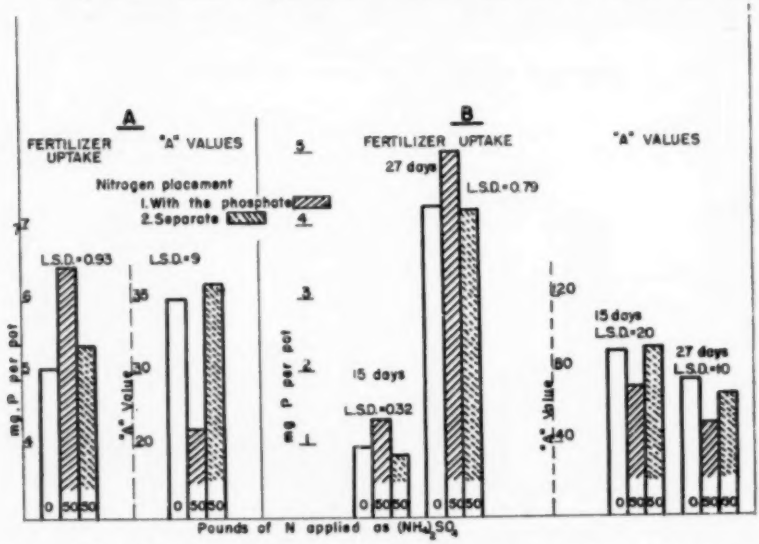


FIG. 3. Effect of nitrogen placement on fertilizer phosphorus uptake and 'A' values by barley grown in the greenhouse. A. Nitrogen mixed with the top 4 in. of soil *vs.* added together with $NH_4H_2PO_4$ at time of seeding. B. Nitrogen added in solution together with, and separate from, a solution of $NH_4H_2PO_4$ after emergence of seedlings. Harvests were taken 15 and 27 days after fertilization.

experiments are given in Fig. 3. The data presented for experiment A confirm the previous field experiment in that mixing the nitrogen throughout the soil has not significantly altered phosphorus absorption, nor have 'A' values been altered. On the other hand, nitrogen as the ammonium ion when mixed with the phosphorus carrier significantly increased the uptake of phosphorus from the carrier and the calculated 'A' values dropped accordingly.

In the first harvest recorded for Experiment B, taken 15 days after fertilization, the importance of nitrogen placement is already clearly evident. When it is noted that the nitrogen and phosphorus were both placed in the root zone in this experiment, and separated by only 1 in. when added separately, the need for intimate association of the fertilizer nitrogen and phosphorus in order to obtain increased uptake is clearly manifested. The second harvest substantiates these differences in placement.

Comparison of various nitrogen salts and a non-nitrogen acidic salt

In addition to the nitrogen-placement treatments described for the greenhouse experiment A, other treatments were also included to investigate the hypothesis that the increased acidity brought about by addition of acid-forming nitrogen salts accounted for the measured increase in uptake that was obtained. All treatments with the exception of the check where no fertilizer was added received an application of $NH_4H_2PO_4$ at the rate of 24 lb. of P_2O_5 per acre. Two treatments consisted of nitrogen in the form of $(NH_4)_2SO_4$ and KNO_3 applied with the

TABLE 3

The Effect of Adding Acid and Non-acid Salts on the Uptake of Fertilizer Phosphorus by Barley Grown in the Greenhouse

Fertilizer treatments	*Soil* pH *in fertilizer band*	*Plant wt. g./pot*	*Total* P *mg./pot*	*Fert.* P *mg./pot*	*'A' value*
Check	7·26	4·97	10·3	..	..
$NH_4H_2PO_4$ at 24 lb. P_2O_5/Ac. .	7·16	5·89	12·5	5·08	35
$NH_4H_2PO_4$ at 24 lb. P_2O_5/Ac. plus $KHSO_4$ . . .	5·89	6·01	12·8	4·06	52
$NH_4H_2PO_4$ at 24 lb. P_2O_5/Ac. plus NH_4SO_4 at 50 lb. N/Ac.	5·97	6·64	13·5	6·44	26
$NH_4H_2PO_4$ at 24 lb. P_2O_5/Ac. plus KNO_3 at 50 lb. N/Ac. .	7·16	6·47	13·2	5·46	34
L.S.D.	0·16	0·84	0·34	0·93	9

phosphorus at 50 lb. of N per acre. To test the effect of acidity a third treatment, an acid salt, $KHSO_4$, was mixed with the phosphorus carrier at a rate calculated to produce an acidity equivalent to the $(NH_4)_2SO_4$. In calculating the acidity of the $(NH_4)_2SO_4$ it was assumed that all the nitrogen would be converted to nitrates. After emergence of the crop an amount of K_2SO_4, equal to the highest rate of potassium used, was applied in solution to each crock. Where the fertilizer added already contained potassium, the amount of K_2SO_4 added was reduced accordingly. The pH in the vicinity of the fertilizer band was measured after harvesting the crop.

The results for this experiment are summarized in Table 3. Addition of either $KHSO_4$ or $(NH_4)_2SO_4$ significantly reduced the pH in the vicinity of the fertilizer band. Nitrogen, added as the ammonium ion, increased uptake and reduced the 'A' value in the usual manner. On the other hand, addition of nitrogen in the nitrate form was ineffective. Mixing the acid salt, $KHSO_4$, with the $NH_4H_2PO_4$ did not bring about the expected increase in uptake, but rather a reduction in phosphorus uptake and an increase in the 'A' value were recorded. This decreased absorption might be explained by the toxicity of the acid salt, as the $KHSO_4$ would produce an immediate reduction in pH in the fertilizer band. This is in contrast to the slow pH drop that would be expected where $(NH_4)_2SO_4$ was used. It has been shown (Arnon, 1939); Stahl

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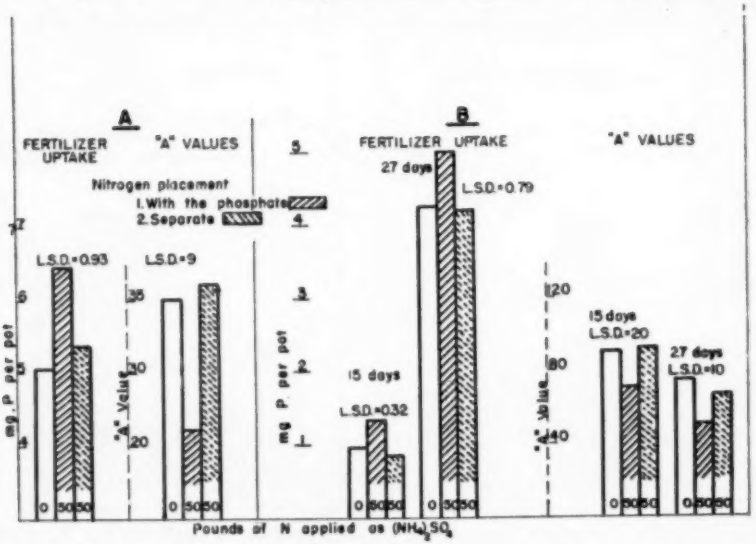

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and Shive, 1933) that damage to roots of crops in solution cultures may occur when the pH drops below 4. If there was root damage with the $KHSO_4$ and subsequent impairment of root development, it would explain the results obtained. However, growth interferences due to the $KHSO_4$ were not evident in determinations other than fertilizer phosphorus uptake.

Further effects of acidity were measured in field experiments on Melfort silty clay loam soil during the 1954 growing season. A fallow-plot site was selected in order that growth responses to added nitrogen

TABLE 4

The Uptake of Fertilizer Phosphorus by Barley grown for 33 and 53 Days in the Field.

(Fertilizers used included Mono-ammonium Phosphate to which Differing Salts were added)

Treatments	*33 days growth*			*35 days growth*		
	Total P *mg./16 ft. row*	*Fert.* P *mg./16 ft. row*	*'A' value*	*Total* P *mg./16 ft. row*	*Fert.* P *mg./16 ft. row*	*'A' value*
1. Check	116	..	..	492	..	..
2. $NH_4H_2PO_4$ at 24 lb. P_2O_5 per acre	197	76	38	510	145	61
3. $NH_4H_2PO_4 + KHSO_4$	140	44	57	447	83	107
4. $NH_4H_2PO_4 + KHSO_4$ ($\frac{1}{4}$)	186	63	48	528	119	83
5. $NH_4H_2PO_4 + (NH_4)_2SO_4$	264	142	21	519	176	47
6. $NH_4H_2PO_4$ + Urea	282	128	29	546	181	49
7. $NH_4H_2PO_4 + KNO_3$	246	101	34	581	162	63
L.S.D.	42	10	7	N.S.	26	8

would not complicate the data obtained. Field-plot techniques were the same as those outlined previously, with the exception that a randomized-block design was used for the seven treatments. These plots were replicated to allow for two dates of harvest. The treatments, along with the dates of harvest, are listed in Table 4. The nitrogen sources, $(NH_4)_2SO_4$, urea, and KNO_3, were applied at 30 lb. of N per acre, and in addition two rates of $KHSO_4$ were used, one equivalent to $(NH_4)_2SO_4$ in acidity, and the other applied at one quarter of this rate. All additions were mixed with the phosphorus fertilizer, $NH_4H_2PO_4$, and applied with the seed.

The spring growing conditions were particularly cold and damp and probably resulted in the nitrogen deficiency that was apparent on this fallow plot. This would explain the greater yield of total phosphorus that resulted from the addition of nitrogen.

The fertilizer uptake and 'A'-value data obtained from this field experiment correlate closely with that obtained previously in the greenhouse. The nitrogen salts containing the ammonium ion, $(NH_4)_2SO_4$, and urea gave the greatest increases in uptake of fertilizer phosphorus, this increased uptake being reflected in a significant drop in 'A' values

for both harvests. The nitrate-nitrogen carrier, KNO_3, did increase fertilizer uptake, but only in so far as the nitrogen itself stimulated the growth of a larger plant. However, 'A' values for this latter treatment are not statistically different from that for $NH_4H_2PO_4$ alone. The addition of the acid salt $KHSO_4$, at both rates used, again resulted in a decrease in adsorption of fertilizer phosphorus, and a rise in 'A' values.

These experiments designed to simulate the acid-forming effects of ammonium salts by adding an acid salt, $KHSO_4$, to the phosphorus carrier have indicated that increased acidity in the fertilizer band may

TABLE 5

The Comparative Effect of Doubling the Rate of Application of Phosphorus, or Addition of the Ammonium Ion, on the Uptake of Phosphorus by Barley Plants grown in the Greenhouse for 15 and 27 Days after Fertilization

Treatment	*15 days*			*27 days*		
	Total P *mg./pot*	*Fert.* P *mg./pot*	*'A' value*	*Total* P *mg./pot*	*Fert.* P *mg./pot*	*'A' value*
1. Check	3·5	..	..	14·2	..	..
2. KH_2PO_4 at 24 lb. P_2O_5 per acre	4·5	0·96	91	17·5	4·26	75
3. KH_2PO_4 at 48 lb. P_2O_5 per acre	4·4	0·99	168	17·5	5·33	110
4. KH_2PO_4 at 24 lb. P_2O_5 per acre plus $(NH_4)_2SO_4$ at 30 lb. N per acre	5·2	1·33	71	15·6	5·00	51
5. KH_2PO_4 at 24 lb. P_2O_5 per acre plus KNO_3 at 30 lb. N per acre	4·0	0·85	92	17·0	4·59	65
L.S.D. ($P = 0·05$)	1·0	0·25	22	2·1	0·57	10

not account for the role of nitrogen in promoting fertilizer phosphorus uptake. Either acidity has no effect in increasing phosphorus availability, or this acid salt has exerted an adverse effect on absorption of phosphorus. Further information was obtained on this question in two greenhouse experiments conducted during the winter of 1954–5.

The data listed in Table 5 were obtained from a greenhouse experiment designed to compare, at various stages of plant growth, the phosphorus uptake obtained from an application of 24 lb. per acre of P_2O_5 (in the form of KH_2PO_4) with and without added $(NH_4)_2SO_4$, with that obtained from an application of 48 lb. per acre of P_2O_5. It has been shown in Fig. 1 that doubling the rate of phosphorus application creates a condition where approximately twice the amount of available phosphorus is present. A check on any nutritive value of the nitrogen was afforded by adding a further treatment including a mixture of KNO_3 and KH_2PO_4. The fertilizers were added in solution after the two-leaf stage in a manner previously outlined for the Experiment 'B' placement studies. Harvests were taken at 15 and 27 days after application of the fertilizer.

In the first harvest, making the phosphorus comparatively more available by doubling the amount added has not increased the amount of fertilizer phosphorus taken up by the plant over that of the 24 lb. per acre application. The addition of $(NH_4)_2SO_4$ did, however, significantly increase the amount of fertilizer phosphorus absorbed by the barley. This early stimulation in fertilizer uptake cannot, therefore, be attributed to an increase in availability of the phosphorus in the carrier, but must reflect an interaction between the ammonium and phosphorus ions that has resulted in an increased absorption of phosphorus by the barley.

TABLE 6

The Effect of Nitrogen and Phosphorus Fertilization on the Nitrogen Uptake by Barley Grown in the Greenhouse for 25 days

Fertilizer treatments	*Plant wt. g./pot*	*Total N mg./pot*	% N
1. Check	2·07	69·1	3·34
2. KH_2PO_4 at 24 lb. P_2O_5 per acre	2·19	70·0	3·19
3. KH_2PO_4 at 24 lb. P_2O_5 per acre plus $(NH_4)_2SO_4$ at 50 lb. N per acre	2·55	102·7	4·02
4. KH_2PO_4 at 24 lb. P_2O_5 per acre plus KNO_3 at 50 lb. N per acre	2·20	91·4	4·15
5. KH_2PO_4 at 24 lb. P_2O_5 per acre plus $(NH_4)_2SO_4$ at 50 lb. per acre applied separately 1 in. below the seed level	2·40	99·0	4·23
L.S.D.	0·17	5·4	0·23

Twenty-seven days after fertilization the 48-lb. rate of P_2O_5 has significantly increased the amount of fertilizer phosphorus taken up over the 24-lb. rate of application. Except for this treatment, the results are quite similar to those of the first harvest.

Since this increase in phosphorus absorption is detectable in the early stages of plant growth and is realized only where nitrogen in the ammonium form is intimately mixed with the phosphate carrier, it was thought that possibly the increased phosphorus absorption may be accompanied by a similar increase in nitrogen uptake by the young plants. With this in mind a greenhouse experiment was set up using the same fertilizer treatments as the preceding experiment with the exception that the 48 lb. per acre rate of KH_2PO_4 was omitted. All fertilizers were applied at the time of seeding. The plants were harvested 25 days after seeding, this period of growth being comparable to the first harvest taken for the previous experiment where the plants were harvested 15 days after fertilization. The data obtained are presented in Table 6.

Increases in total plant weight over the check were realized for all fertilizer treatments, but by far the greatest increase was obtained where the ammonium source of nitrogen was mixed with the KH_2PO_4. Where the $(NH_4)_2SO_4$ was separated from the phosphorus a drop in yield was recorded compared to that where both were intimately mixed and applied with the seed. The lowered uptake of fertilizer phosphorus in the former treatment probably is responsible for this difference in yield.

The addition of nitrate nitrogen to the phosphorus carrier resulted in a yield identical with that where the phosphorus alone was applied.

Phosphorus fertilization alone did not alter the yield of total nitrogen. Mixing either $(NH_4)_2SO_4$ or KNO_3 with the phosphorus carrier, or placing $(NH_4)_2SO_4$ separately, resulted in highly significant increases over the check or phosphorus alone; the $(NH_4)_2SO_4$, regardless of placement, significantly increased the yield of nitrogen over and above that of the KNO_3. It is rather significant that phosphorus placement with respect to the nitrogen fertilizer has no effect on uptake of total nitrogen, since the reverse, nitrogen placement versus phosphorus uptake, is very important.

These data indicate that young barley plants take up large amounts of nitrogen from an ammonium source, in preference to that of a nitrate source. Placement of nitrogen with respect to the phosphorus had little effect on total nitrogen uptake. If the amount of nitrogen taken up from the added $(NH_4)_2SO_4$ is assumed to be the difference between the total nitrogen of the sulphate treatment and the check, then approximately 60 per cent. of the applied nitrogen was utilized 25 days after seeding. It is not unreasonable to expect that this large absorption of nitrogen would have an effect on fertilizer phosphorus uptake when the two ions are closely associated in the fertilizer band.

Discussion and Conclusion

From the data reported, an increase in fertilizer-phosphorus absorption by plants was shown to have occurred where nitrogen, as the ammonium ion, was mixed with the phosphorus carrier. This increase in uptake was proportionately greater for the first increments of nitrogen added, but continued stimulation in uptake occurred throughout the range used, 10, 20, and 40 lb. of nitrogen per acre. Nitrate sources of nitrogen were relatively ineffective in increasing phosphorus-fertilizer utilization, and any increase in uptake recorded for the nitrate phosphorus mixtures can be attributed to the nutritional effect of the nitrogen which resulted in increased growth.

The addition of the ammonium ion as a top-dressing treatment, or mixed uniformly through the surface soil, or added in solution approximately one inch from the phosphorus carrier, did not appreciably alter phosphorus absorption. Increased utilization of phosphorus was realized only when the ammonium nitrogen was intimately associated with the phosphorus fertilizer.

The stimulative effect of added ammonium nitrogen on phosphorus uptake was shown to occur at a very early stage of growth; in one experiment, significant increases in uptake were recorded 15 days after fertilization.

The increase in uptake of the phosphorus fertilizer when mixed with ammonium nitrogen does not correlate, in the early stages of plant growth, with the amount of available phosphorus present in the fertilizer band, as greater uptake of fertilizer phosphorus was obtained from a 24 lb. per acre application of P_2O_5 to which 30 lb. of nitrogen had been added as $(NH_4)_2SO_4$, than where 48 lb. per acre of P_2O_5 were applied.

From this work, to date, no single hypothesis can be formulated which will fully explain why plant utilization of fertilizer phosphorus is enhanced by the ammonium nitrogen. The initial supposition (Rennie and Mitchell, 1954), that acid-forming ammonium salts such as NH_4NO_3 would reduce fixation of the fertilizer phosphorus in the soil, thus prolonging the availability of the dissolved phosphorus, does not appear to be a satisfactory theory for two reasons. Firstly, the addition of an acid salt, $KHSO_4$, in greenhouse and field experiments, to phosphorus carriers did not increase the uptake of phosphorus, but rather significantly decreased it. Secondly, the increased uptake of phosphorus due to the ammonium ion has been shown to occur in an early stage of plant growth, and not at a later stage which might be expected if acidity played a major role.

It would appear from this work that the ammonium ion influences the plant's ability to take up phosphorus, rather than altering, in any way, the availability of the applied phosphorus.

This explanation finds some support in work on absorption and assimilation of ammonium and nitrate nitrogen by plants. Stahl and Shive (1933), working with oats in solution culture containing ammonium and nitrate nitrogen, report that ammonium-nitrogen absorption is highest during the early stages of plant growth and reaches a very low rate with approaching maturity. The rate of absorption of nitrate nitrogen is low during the early stages of growth and at a maximum at the blossoming stage. The maximum ammonium rate of absorption is double the maximum nitrate rate. This preferential absorption of ammonia over nitrate ions has been shown in this study to correlate with the increased uptake of phosphorus. Arnon (1939) and Breon *et al.* (1944) also report a similar relationship between the absorption of phosphorus and ammonium ions.

It can, therefore, be concluded that there is a close relationship between the high absorption of ammonium ions and the increased uptake of fertilizer phosphorus, both of which occur during the early stages of plant growth. The ammonium ion is probably the dominant factor, as phosphorus was shown in this work to have little effect on nitrogen absorption. Rapid ammonium-ion absorption appears to be accompanied or followed by enhanced phosphorus absorption when both ions are closely associated in the fertilizer band.

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